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A Phase-Space Electronic Hamiltonian For Vibrational Circular Dichroism

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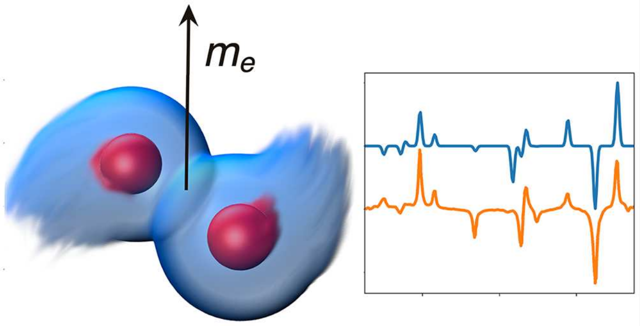
ABSTRACT: We show empirically that a phase-space non-Born−Oppenheimer electronic Hamiltonian approach to quantum chemistry (where the electronic Hamiltonian is parametrized by both nuclear position and momentum, $\hat{\boldsymbol{H}}_{PS}(\boldsymbol{R},\boldsymbol{P})$) is both a practical and accurate means to recover vibrational circular dichroism spectra. We further hypothesize that such a phase-space approach may lead to very new dynamical physics beyond spectroscopic circular dichroism, with potential implications for understanding chiral induced spin selectivity (CISS), noting that classical phase-space approaches conserve the total nuclear plus electronic momentum, whereas classical Born−Oppenheimer approaches do not (they conserve only the nuclear momentum).



1. INTRODUCTION: CHIRALITY AND CIRCULAR DICHROISM

Molecular chirality occurs whenever a system lacks any inversion or mirror symmetry. Such systems have long fascinated chemists, going all the way back to the work of Pasteur more than 150 years ago.[1] Chirality continues to be a target of cutting-edge research, with the 2021 Nobel Prize in Chemistry being awarded for chiral synthesis[2,3] and the current explosion of interest in chiral-induced spin selectivity,[4−6] the effect whereby electronic conduction through a chiral medium is found to be spin-polarized. One hypothesis for explaining the chiral induced spin selectivity (CISS) effect is that coupled nuclear-electronic motion transfers angular momentum from "chiral phonons"[7,8] to electronic spin degrees of freedom—although this hypothesis is unconfirmed and many details remain uncertain.[9−11] Nevertheless, what is clear is that the chirality of a molecular system can substantially affect electronic properties in ways we still do not fully understand and cannot control.

To date, the standard approach in the literature for identifying and characterizing chiral molecules and materials is to use circular dichroism (CD) spectroscopy, which measures the differential absorption of molecular systems to circularly polarized light. While nonchiral molecules respond equivalently to both left and right circularly polarized light, the response of chiral molecules is reversed based on the enantiomer.[12] In particular, because they lack inversion or mirror symmetry, chiral molecules display different magneto-electronic responses, which leads to a small difference in absorption when exposed to left-handed and right-handed circularly polarized light. Over the last few decades, in order to treat chirality in different regimes, experimentalists have designed various flavors of CD spectroscopy, electronic circular dichroism (ECD),[13] vibrational CD (VCD),[14] magnetic CD (MCD),[15] magnetic vibrational CD (MVCD), X-ray magnetic CD (XMCD), Raman optical activity (ROA), etc. Effectively, one can measure the differential absorption of molecules in many wavelength regimes (from radio-wave to X-ray) and in many environments (e.g., including or not including magnetic fields, solvated and unsolvated).

In order to interpret the different CD spectroscopies listed above, the job of the theoretical chemist is usually to calculate the rotatory strength $\mathcal{R}$, which is related to the difference in left-handed vs right-handed absorption when averaged over all incoming directions of light and molecular geometries. Mathematically, this difference in molecular absorption can be quantified using the product of an electronic transition matrix element ($\boldsymbol{\mu}$) dotted into a magnetic transition matrix element ($\boldsymbol{m}$):

$$\mathcal{R} = \mathrm{Im}(\boldsymbol{\mu}_{if} \cdot \boldsymbol{m}_{fi}) \tag{1}$$

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where i and f represent the initial and final states, before and after absorption of a photon. One can find many review articles discussing the strategies for calculating $\mathcal{R}$[16−21] as well as below (Section 2.5). Historically, one of the difficulties encountered when calculating the rotatory strength is that, because we are limited to a finite basis, magnetic response properties will naively depend on the choice of origin.

1.1. Vibrational Circular Dichroism and Magnetic Field Perturbation Theory.

It is crucial to emphasize that calculating $\mathcal{R}$ for each of the different CD spectroscopies above can require quite different methodologies. In particular, relative to the ECD signal, the calculation of a VCD signal can be much less straightforward because, within Born−Oppenheimer theory, the electronic contribution to the magnetic transition dipole moment vanishes between any vibrational modes i and f.[22] To see why this is so, note that the BO Hamiltonian is time-reversible, so that all nondegenerate eigenstates are also time-reversible (with zero average electronic momentum, $\langle \hat{\boldsymbol{p}} \rangle = \langle \hat{\boldsymbol{m}} \rangle = 0$). This inability of standard BO theory to calculate VCD spectra stimulated the original work of Nafie to go beyond BO theory and construct the relevant nonzero matrix elements between perturbatively corrected BO states.[23] At present, there are two main approaches:

(i) The first and less common approach invokes a sum over excited states (SOS)[24] in order to generate a perturbatively correct mixed electronic-nuclear wave function within a basis of BO wave functions.

(ii) The second and now more common approach was formulated by Stephens and Buckingham, which computes the orbital response to a magnetic field perturbation (MFP),[19,25] which formally recovers the same sum over excited states but in a more tractable manner.

For VCD (as for most vibrational problems), one quantifies the electric dipole component of eq 1 by expanding the ground-state electronic dipole in nuclear position and then quantizing and taking matrix elements of the nuclear position operator:

$$\hat{\boldsymbol{\mu}} = \boldsymbol{\mu}(\mathbf{R}^{\mathrm{eq}}) + \sum_{\mathrm{A}\alpha} \frac{\partial \hat{\boldsymbol{\mu}}}{\partial R_{\mathrm{A}\alpha}}(\hat{R}_{\mathrm{A}\alpha} - R_{\mathrm{A}\alpha}^{\mathrm{eq}}) + ... \tag{2}$$

In principle, one would like to expand and evaluate the magnetic transition moment, $\boldsymbol{m}$, in a similar fashion—but, as just discussed, within the BO approximation, $\boldsymbol{m} = \mathbf{0}$ (and so are all spatial derivatives of $\boldsymbol{m}$, $\frac{\partial \boldsymbol{m}}{\partial \mathbf{R}} = 0$). That being said, the insight of Nafie and Stephens was that, as the nuclei move, that motion induces electronic motion, which should allow an expansion of the magnetic transition moment, $\boldsymbol{m}$, in terms of a nuclear canonical momentum (where $\mathbf{P}_A^{\mathrm{eq}} = 0$):

$$\hat{\boldsymbol{m}} = \sum_{\mathrm{A}\alpha} \frac{\partial \hat{\boldsymbol{m}}}{\partial P_{\mathrm{A}\alpha}}(\hat{P}_{\mathrm{A}\alpha} - P_{\mathrm{A}\alpha}^{\mathrm{eq}}) + ... \tag{3}$$

The success of the MFP approach is that one can map $\frac{\partial \boldsymbol{m}}{\partial P}$ to a double response function calculation (see eq 90 below). Now, in principle, one might ask: why intuitively should it be more difficult or involved to calculate a VCD spectrum relative to an IR or ECD spectrum? Why does the calculation of $\frac{\partial \boldsymbol{m}}{\partial P}$ require a double perturbation in eq 90, whereas the calculation of $\frac{\partial \boldsymbol{\mu}}{\partial R}$ requires only a single perturbation (see eq 59)? Just as IR spectra can be interpreted by performing a Fourier transform on the dipole−dipole correlation function, can we interpret VCD spectra as evolving from dynamics on a non-BO surface? In short, is there a non-BO approach that can put VCD theory in a less esoteric framework?

In a sense, Nafie asked these questions long ago, which led him to introduce nuclear velocity perturbation theory, whereby one introduces gauges to the atomic orbitals[26] in an attempt to capture how electronic wave functions depend self-consistently on nuclear velocity and fashion a more natural treatment of VCD. Unfortunately, the need for multiple orbital response calculations leads to an expensive algorithm, and so the nuclear velocity perturbation (NVP) approach has not been studied in as much detail over the years. Nevertheless, Nafie laid the groundwork for future nonadiabatic methods designed to recover VCD spectra. And recently, the community has taken up the cause and shown progress with NVP.[27,28] In this paper, we will take a different approach and show that VCD spectra can easily be interpreted through a simple and intuitive phase-space approach to electronic structure theory.

1.2. Phase-Space Electronic Hamiltonian Approaches and an Outline of This Paper.

The essence of our phase-space electronic Hamiltonian approach is to avoid the Born−Oppenheimer framework and directly parametrize the electronic Hamiltonian by both position and momentum, $H_{\mathrm{PS}}(\boldsymbol{R},\boldsymbol{P})$. As a sidenote, the phrase "phase space" in quantum mechanics has a long history dating back the early work of Wigner, Weyl, and Moyal, who showed that quantum dynamics can be performed exactly within a phase-space formalism.[29,30] Moreover, within the context of nonadiabatic dynamics, there have been several attempts to map the dynamics of a set of electronic states to a set of classical equations[31−33] and then use phase-space techniques to simulate the trajectory-based quantum dynamics of a set of nuclear degrees of freedom (as written about extensively by Liu[34]). To differentiate our approach (which is really a choice of electronic basis but not at all a method for nuclear quantum dynamics) from the latter techniques (which seek nonadiabatic solutions), henceforward we will consistently speak of "phase-space electronic Hamiltonian" approaches (rather than just a generic "phase-space" approach).

Recently, we proved that, if one runs classical nuclear dynamics along the eigensurfaces of a properly constructed phase-space electronic Hamiltonian, $H_{\mathrm{PS}}(\boldsymbol{R}, \boldsymbol{P})$, one indeed conserves the total linear and angular momentum;[35] by contrast, for systems with odd numbers of electrons, classical BO dynamics violates momentum conservation (unless a Berry force is included[36,37]). Moreover, as argued originally by Shenvi (based heuristically on earlier work of Micha[38] and more direct work of Berry on superadiabats[39,40]), nonadiabatic surface hopping algorithms are most natural with phase-space electronic Hamiltonian surfaces. Indeed, in the context of intersystem crossing (ISC) and/or problems with spin degeneracy,[41] standard surface hopping must be adjusted because momentum rescaling is not well-defined if the rescaling direction is complex-valued. For these reasons, phase-space electronic Hamiltonian methods represent a very attractive tool to explore electron−phonon couplings, especially in the context of problems with spin dependent Hamiltonians. (Interestingly, among those chemists and physicists seeking to build a non-Born−Oppenheimer framework to nonadiabatic dynamics without any mapping techniques, most of the focus nowadays is on exact factorization methods[42−46]—which are also attractive methods that conserve momentum[47] but algorithmically require tools even farther away from standard BO theory than simple phase-space methods.)

With this background in mind, the goal of the present paper is to directly validate a phase-space electronic structure Hamiltonian approach by comparing against experimental VCD spectra for a series of small rigid molecules. Note that, in this manuscript, we will not propagate nonadiabatic trajectories of any kind; in particular, although below we will motivate the notion of a phase-space electronic Hamiltonian from the perspective of semiclassical dynamics, there will be no surface hopping results of any kind. Instead, our goal is to empirically establish whether the eigenstates of the heuristic Hamiltonian presented below (in eq 27) match up well with experimental data. This article is structured as follows. In Section 2.1, we review the approximations taken in the standard BO approach to nonadiabatic theory. In Section 2.2, we review the basic theory of phase-space electronic Hamiltonians, highlighting the essential equations needed for momentum conservation. In Section 2.3, we discuss a second derivative coupling we have recently implemented. In Section 2.4, we discuss how to construct normal modes in a phase-space framework. In Section 2.5 we discuss the form of the rotational strength in the phase-space framework. Finally, in Section 2.6, we define the transition electric and magnetic dipole moments at our level of theory. Thereafter, in Section 3, we present our results which strongly validate phase-space electronic structure theory (at least numerically). Lastly, in Section 4, we interpret our findings and speculate on their implications for dynamics beyond VCD theory.

Before concluding this introduction, a word about notation is in order. Henceforward,

- Roman letters I, J, and K denote adiabatic states
- $\{\mu, \nu, \lambda, \sigma\}$ index atomic orbitals $\{\chi_\mu, \chi_\nu, \chi_\lambda, \chi_\sigma\}$
- $\{\alpha, \beta, \gamma, \delta\}$ index the x,y,z Cartesian directions
- Greek letters $\{\tau, \kappa, \eta, \theta\}$ index spin of molecular orbital coefficients
- A, B, ... index atomic centers
- Bold font indicates three-dimensional quantities (operators or c-numbers)
- Hats indicate operators (nuclear and electronic).
- $\boldsymbol{R}_\mathrm{A}$ and $\boldsymbol{P}_\mathrm{A}$ denote the three-dimensional position and momentum for nucleus A, while $\boldsymbol{R}$ and $\boldsymbol{P}$ denote a 3N-dimensional vector for all nuclear positions and momenta.
- Adiabatic wave functions are denoted by Φ_J, with corresponding nuclear wave function Ω_J.
- k indexes normal modes
- The charge of an electron is denoted $-e$ (i.e., we fix $e > 0$).

2. THEORY: A PHASE-SPACE ELECTRONIC HAMILTONIAN FRAMEWORK

2.1. Standard Born-Oppeneimer Approach to Non-adiabatic Theory.

To understand how phase-space electronic Hamiltonians can be rationalized, consider the standard quantum mechanical molecular Hamiltonian

$$\hat{H}_\mathrm{tot} = \hat{T}_\mathrm{nuc} + \hat{H}_\mathrm{el} \tag{4}$$

where $\hat{\boldsymbol{T}}_\mathrm{nuc}$ is the kinetic nuclear energy operator (that depends on canonical momentum $\boldsymbol{P}$) and $\hat{\boldsymbol{H}}_\mathrm{el}$ is the electronic Hamiltonian (that depends on $\boldsymbol{R}$). According to standard Born−Oppenheimer theory, in order to model dynamics, one first diagonalizes the electronic Hamiltonian $\hat{\boldsymbol{H}}_\mathrm{el}$,

$$\hat{H}_\mathrm{el}|\Phi_K\rangle = E_K(\mathbf{R})|\Phi_K\rangle \tag{5}$$

Second, one expresses the combined nuclear-electronic wave function $\Psi(\boldsymbol{r}, \boldsymbol{R})$ in the basis of adiabatic states:

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_J \Phi_J(\mathbf{r}; \mathbf{R})\Omega_J(\mathbf{R}) \tag{6}$$

In such a representation, using the fact that $\hat{T}_\mathrm{nuc} = -\sum_\mathrm{A} \frac{\hbar^2}{2M_\mathrm{A}} {\nabla_{R_\mathrm{A}}}^2$, it is straightforward to show that the Hamiltonian takes the following form:

$$\hat{H}_\mathrm{tot} = \sum_{IJK} \frac{1}{2M}|\Phi_I\rangle(\hat{P}\delta_{IJ} - i\hbar\mathbf{d}_{IJ})\cdot(\hat{P}\delta_{JK} - i\hbar\mathbf{d}_{JK})\langle\Phi_K| + \sum_k E_{KK}(\hat{\mathbf{R}})|\Phi_K\rangle\langle\Phi_K| \tag{7}$$

where $\hat{P} = \frac{\hbar}{i}\frac{\partial}{\partial\mathbf{R}}$ in the position basis. Note that, after an adiabatic transformation of this kind, one has entangled the electronic Hamiltonian and the nuclear kinetic energy. Nevertheless, it is still common to write

$$\hat{H}_\mathrm{tot} = \hat{T}_\mathrm{nuc}^\mathrm{ad} + \hat{H}_\mathrm{el}^\mathrm{ad} \tag{8}$$

where, if $\hat{\mathrm{U}}$ is the matrix of adiabatic eigenvectors expressed in a diabatic basis, $\hat{\boldsymbol{T}}_\mathrm{nuc}^\mathrm{ad} = U^\dagger\ \hat{\boldsymbol{T}}_\mathrm{nuc}\ U$ and $\hat{\boldsymbol{H}}_\mathrm{el}^\mathrm{ad} = U^\dagger\ \hat{\boldsymbol{H}}_\mathrm{el}\ U$.

Equation 7 is exact (without any approximation). Inevitably, however, in order to simulate a real system, one is forced to make approximations and the most common initial step is to assume that all nuclear motion will be classical. In that vein, the surface hopping[48,49] view of nonadiabatic dynamics is that one interprets dynamics following the Hamiltonian in eq 7 as arising from two steps:

- Propagate classical motion along potential energy surface K (as represented by the operator $\hat{\boldsymbol{H}}_\mathrm{el}^\mathrm{ad}(\hat{\boldsymbol{R}})$).
- Hop probabilistically between potential energy surfaces, J and K (as represented by the $\hat{\boldsymbol{P}}\cdot\boldsymbol{d}_{JK}$ operator).

This view of nonadiabatic motion, based on the separation between the $\hat{\boldsymbol{T}}_\mathrm{nuc}^\mathrm{ad}$ and $\hat{\boldsymbol{H}}_\mathrm{el}^\mathrm{ad}$ terms in eq 8, clearly depends delicately on the choice of electronic basis. For the most part, surface hopping is only well-defined in an adiabatic basis—even though exact quantum dynamics has no preferred basis.[50] Nevertheless, this surface hopping approach has been validated for many Hamiltonians.

2.2. Intuition behind a Phase-Space Approach.

Beginning with Shenvi's seminal work,[51] the original rationale for a phase-space surface hopping formalism was that if one were to partition the Hamiltonian slightly differently from eq 8, one could go beyond BO theory by entangling nuclear and electronic motion both through hops *and* along dynamics on one surface. To that end, if one is prepared to run a classical simulation, Shenvi proposed rediagonalizing the full Hamiltonian which is parametrized by both $\boldsymbol{R}$ and $\boldsymbol{P}$:

$$\hat{H}_\mathrm{Shenvi}(\mathbf{R}, \mathbf{P}) = \sum_{IJK\mathrm{A}} \frac{1}{2M_\mathrm{A}}(\mathbf{P}_\mathrm{A}\delta_{IJ} - i\hbar\mathbf{d}_{IJ}^\mathrm{A})\cdot(\mathbf{P}_\mathrm{A}\delta_{JK} - i\hbar\mathbf{d}_{JK}^\mathrm{A})|\Phi_I\rangle\langle\Phi_K| + \sum_k E_{KK}(\mathbf{R})|\Phi_K\rangle\langle\Phi_K| \tag{9}$$

$$\hat{H}_{\mathrm{Shenvi}}(\mathbf{R},\mathbf{P})\Psi_{\mathrm{Shenvi}}(\mathbf{R},\mathbf{P}) = E_{\mathrm{Shenvi}}(\mathbf{R},\mathbf{P})\Psi_{\mathrm{Shenvi}}(\mathbf{R},\mathbf{P}) \tag{10}$$

Note that, in eq 9, we have used the mixed quantum-classical representation to replace $(\hat{\boldsymbol{R}},\hat{\boldsymbol{P}})$ with their classical counterparts $(\boldsymbol{R},\boldsymbol{P})$. As shown in several papers,[51,52] for some model problems, dynamics along the phase-space adiabats in eq 10 can produce strong results. Unfortunately, there are several problems:

- The algorithm is not stable. For instance, near a conical intersection, where the derivative coupling diverges, the phase-space adiabatic energies (i.e., the eigenvalues of $\hat{\boldsymbol{H}}_{\mathrm{Shenvi}}$) will also diverge.
- For problems with spin, the eigenstates in eq 5 have some an arbitrary gauge (i.e., phase). The derivative couplings in eq 9 are gauge-dependent, and thus the algorithm is not well-defined.
- The algorithm in practice is quite expensive because, in order to propagate $\frac{\partial E_{\mathrm{Shenvi}}}{\partial \mathbf{R}}$, one must differentiate the deriative coupling—which is at least (if not much more) costly than a second-derivative calculation.

For all of these reasons, Shenvi's direct approach has never been used for large or ab initio systems. Nevertheless, we have argued[35] that there is another, simpler phase-space approach which should capture some of the key physics in eq 9 but without any of the problems listed above. The basic idea of our phase-space approach is rooted in the fact that every calculation of the derivative coupling[53,54] in an atomic orbital basis can always be decomposed into two terms:

$$\left\langle I\left|\frac{\partial}{\partial R_{\mathrm{A}\alpha}}\right|J\right\rangle = d_{IJ}^{\mathrm{A}\alpha} = d_{IJ}^{\mathrm{A}\alpha,\mathrm{ETF}} + \tilde{d}_{IJ}^{\mathrm{A}\alpha} \tag{11}$$

The first term on the right-hand of eq 11 is the electron translation factor (ETF) term,[53] which is defined by

$$d_{IJ}^{\mathrm{A}\alpha,\mathrm{ETF}} = \sum_{\mu\nu}\frac{1}{2}\left(\langle\chi_\mu|\frac{\partial}{\partial R_{\mathrm{A}\alpha}}\chi_\nu\rangle - \langle\chi_\nu|\frac{\partial}{\partial R_{\mathrm{A}\alpha}}\chi_\mu\rangle\right)D_{\mu\nu} \tag{12}$$

where $D_{\mu\nu}$ is the one-particle density matrix. (For a standard Hartree–Fock or Kohn–Sham DFT calculation, with molecular orbitals $c_{\mu i}$, one defines $D_{\mu\nu} = \sum_i^{n_{\mathrm{orb}}} c_{\mu i}c_{\nu i}^{*}$.) In this separation, it is crucial to emphasize that whereas $\boldsymbol{d}_{IJ}$ diverges near a conical intersections, $\boldsymbol{d}_{IJ}^{\mathrm{ETF}}$ is always small, even near a conical intersection; more precisely, although the size of the former depends on the inverse of the energy difference between electronic states, the size of the latter does not. Moreover, because the atomic orbital basis $\{\chi_\mu\}$ is always chosen to be real-valued, there is no phase problem in isolating the term $\boldsymbol{d}_{IJ}^{\mathrm{ETF}}$. Third, differentiating such a term is computationally trivial. For all of these reasons, it is clear that if one were to approximate $\boldsymbol{d}$ by $\boldsymbol{d}^{\mathrm{ETF}}$ in eq 9, the resulting phase-space electronic Hamiltonian would appear to be much more stable and tractable.

Now, in Section 1.2 above, we discussed briefly the fact that standard BO dynamics along the surface $E_K(\boldsymbol{R})$ (generated by eq 4) fails to conserve either linear or angular momentum. In brief, because BO dynamics propagate nuclear dynamics along translationally and rotationally invariant potential energy surfaces, these dynamics conserve the *nuclear* linear and angular momentum. At the same time, however, these algorithms ignore the electronic linear and angular momentum and do not conserve the *total* linear or angular momentum (provided the electronic observables are nonzero). Previously, in refs 35 and,55, we showed that, in order to conserve the total linear and angular momentum along a phase-space adiabat, one can construct a Hamiltonian of the following form:

$$\hat{H}_{\mathrm{PS}} \equiv \sum_{\mathrm{A}\alpha}\frac{P_{\mathrm{A}\alpha}^2}{2M_{\mathrm{A}}} + \hat{H}_{\mathrm{el}} - \sum_{\mu\nu\mathrm{A}\alpha} i\hbar\frac{P_{\mathrm{A}\alpha}}{M_{\mathrm{A}}}\cdot\bar{\Gamma}_{\mu\nu}^{\mathrm{A}\alpha}a_\mu^{\dagger}a_\nu \tag{13}$$

$$\bar{\boldsymbol{\Gamma}}_{\mu\nu}^{\mathrm{A}} \equiv \sum_{\lambda\sigma} S_{\mu\lambda}{}^{-1}\boldsymbol{\Gamma}_{\lambda\sigma}^{\mathrm{A}}S_{\sigma\nu}{}^{-1} \tag{14}$$

provided the $\boldsymbol{\Gamma}$ operators in eq 14 are antisymmetric and satisfy

$$-i\hbar\sum_{\mathrm{A}}\Gamma_{\mu\nu}^{\mathrm{A}\alpha} + p_{\mu\nu}^{\alpha} = 0 \tag{15}$$

$$\sum_{\mathrm{B}}\nabla_{\mathrm{B}\beta}\Gamma_{\mu\nu}^{\mathrm{A}\alpha} = 0 \tag{16}$$

$$-i\hbar\sum_{\mathrm{A}\beta\gamma}\epsilon_{\alpha\beta\gamma}X_{\mathrm{A}\beta}\Gamma_{\mu\nu}^{\mathrm{A}\gamma} + l_{\mu\nu}^{\alpha} + s_{\mu\nu}^{\alpha} = 0 \tag{17}$$

$$\sum_{\mathrm{B}\beta\eta}\epsilon_{\alpha\beta\eta}X_{\mathrm{B}\beta}\langle\mu|\frac{\partial\hat{\Gamma}^{\mathrm{A}\gamma}}{\partial X_{\mathrm{B}\eta}}|\nu\rangle - \frac{i}{\hbar}\langle\mu|[\hat{\Gamma}^{\mathrm{A}\gamma},\hat{L}_e{}^{\alpha}]|\nu\rangle + \sum_{\eta}\epsilon_{\alpha\gamma\eta}\Gamma_{\mu\nu}^{\mathrm{A}\eta} = 0 \tag{18}$$

where $p^{\alpha}{}_{\mu\nu}$ is the linear momentum in the atomic orbital basis, and $l^{\alpha}{}_{\mu\nu}$ and $s^{\alpha}{}_{\mu\nu}$ are the angular momentum and spin matrices in the atomic orbital basis (respectively). Several comments are now in order.

(1) First, note that in eq 14, the S matrix is the overlap matrix. If one had access to a localized, atom-centered orthonormal basis, one could ignore this term entirely (as S would be the identity). In conventional quantum chemistry calculations, however, S is not the identity, and including the S^{-1} factors in eq 14 is one means to ensure that the final energy should involve contractions of the $\boldsymbol{\Gamma}_{\mu\nu}$ matrices. Indeed, if one calculates the expectation value for the operator $\sum_{\mu\nu}\bar{\boldsymbol{\Gamma}}_{\mu\nu}^{\mathrm{A}}a_\mu^{\dagger}a_\nu$ in a state $|\Psi\rangle$, one finds:

$$\begin{aligned}\langle\Psi|\sum_{\mu\nu}\bar{\boldsymbol{\Gamma}}_{\mu\nu}^{\mathrm{A}}a_\mu^{\dagger}a_\nu|\Psi\rangle &= \sum_{\mu\nu\lambda\sigma}\boldsymbol{\Gamma}_{\lambda\sigma}^{\mathrm{A}}S_{\sigma\mu}^{-1}\langle\Psi|a_\mu^{\dagger}a_\nu|\Psi\rangle S_{\nu\lambda}^{-1}\\ &= \sum_{\lambda\sigma}\boldsymbol{\Gamma}_{\lambda\sigma}^{\mathrm{A}}D_{\sigma\lambda}\end{aligned} \tag{19}$$

where $D_{\sigma\lambda}$ is defined in eq 12.

(2) Second, the intuition behind eqs 15–18 is as follows. Equations 15 and 17 are phase conventions that mathematically encapsulate our requirement that electronic wave functions be functions of the electronic coordinates relative to the nuclear coordinates. Thus, eq 15 stipulates that under translation of the nuclei, the electronic wave function will also translate. Equation 17 stipulates that under rotation of the nuclei, the entire electronic wave function will also rotate. Next, eq 16 is a mathematical statement that the $\boldsymbol{\Gamma}$ couplings should effectively be invariant to translations of the molecule,

$\Gamma^{A\alpha}_{\mu\nu}(\boldsymbol{R}_0 + \Delta) = \Gamma^{A\alpha}_{\mu\nu}(\boldsymbol{R}_0)$. Equations 15−17 are closely related to the transformation properties of the basis states and derivative couplings under translations and rotations, as discussed in refs 56 and 57, the main difference being that those papers treat multielectron basis functions rather than atomic orbitals. For example, eqs 15 and 16 are closely related to eqs 172 and 179 of ref 57 and eq 17 is related to eq 107 of ref 56.

In eq 18, the operator $\hat{\Gamma}^{A\gamma}$ can be any operator that satisfies $\langle \mu | \hat{\Gamma}^{A\gamma} | \nu \rangle = \Gamma^{A\gamma}_{\mu\nu}$. Note that the form of eq 18 is slightly involved because, within usual quantum chemistry calculations with atomic orbital basis functions, one does not reorient a given atomic orbital upon rotation. For instance, a p_x orbital is always in the x-direction of the lab frame regardless of the orientation of the molecule. Nevertheless, despite this annoyance, the meaning of eq 18 is clear: the matrix elements must transform correctly to rotations, so the total energy is invariant. In other words, if U is a rotation matrix, eq 18 dictates that $\Gamma^{A\alpha}_{U\mu U\nu}(U\mathbf{R}_0) = \sum_\beta U_{\alpha\beta}\Gamma^{A\beta}_{\mu\nu}(\mathbf{R}_0)$.

(3) Third, if one were to fix $\mathbf{\Gamma}^{A}$ as

$$\mathbf{\Gamma}'^{A}_{\mu\nu} = \frac{1}{2}\left(\langle \chi_\mu | \frac{\partial}{\partial R_{A\alpha}} \chi_\nu \rangle - \langle \chi_\nu | \frac{\partial}{\partial R_{A\alpha}} \chi_\mu \rangle \right) \tag{20}$$

in the spirit of eq 12, one can show that this definition of $\mathbf{\Gamma}^{A}$ satisfies the translational requirements in eqs 15 and 16. However, such a definition does not satisfy eqs 17 and 18 for rotations. However, as demonstrated in ref 35 and recapitulated in Appendix F, one can satisfy all of the necessary requirements by fixing

$$\mathbf{\Gamma}^{A}_{\mu\nu} = \mathbf{\Gamma}'^{A}_{\mu\nu} + \mathbf{\Gamma}''^{A}_{\mu\nu} \tag{21}$$

where we refer to $\mathbf{\Gamma}''^{A}_{\mu\nu}$ as an electron rotational factor (ERF). It should be noted that $\mathbf{\Gamma}^{A}$ in eq 21 does not diverge (just like $\boldsymbol{d}^{A,ETF}_{IJ}$), and therefore this ansatz remains a suitable candidate for an electronic-nuclear momentum coupling term.

Thus, at the end of the day, using a standard electronic Hamiltonian with a one-electron operator $\hat{h}$ and a two electron operator $\hat{\pi}$, the most naive phase-space electronic Hamiltonian (as encoded by the Hamiltonian in eq 13 above) postulates that the molecular energy for a system at positions and momenta $(\boldsymbol{R},\boldsymbol{P})$ is of the form:

$$E_{PS}(\mathbf{R}, \mathbf{P}) = \sum_{A\alpha} \frac{P^2_{A\alpha}}{2M_A} + \sum_{\mu\nu} D_{\nu\mu}\left(h_{\mu\nu} - i\hbar \sum_{A\alpha} \frac{P_{A\alpha}\Gamma^{A\alpha}_{\mu\nu}}{M_A} \right) + \sum_{\mu\nu\lambda\sigma} G_{\nu\mu\sigma\lambda}\pi_{\mu\nu\lambda\sigma} \tag{22}$$

Here, $G_{\nu\mu\sigma\lambda}$ represents the two-electron density matrix in an atomic orbital basis.

2.3. Including a Second-Derivative Coupling.

Unfortunately, we have found that the energy expression in eq 22 is not stable as far as generating VCD spectra, especially for large basis sets. After some bench-marking, our tentative hypothesis is that problems arise if the nuclear kinetic energy

$$\sum_{A\alpha} \frac{P^2_{A\alpha}}{2M_A} - i\hbar \sum_{\mu\nu} D_{\nu\mu} \sum_{A\alpha} \frac{P_{A\alpha}\Gamma^{A\alpha}_{\mu\nu}}{M_A}$$

is not positive definite (as it must be). To that end, given the form of the exact Hamiltonian in eq 7 in an adiabatic representation, we posit that a second-order term is appropriate.

At this point, let us consider the simplest possible system: a single electron interacting with a host of nuclei. In such a situation, second-quantization becomes trivial and equivalent to first quantization, and we hypothesize that one can write down a meaningful analogue of eq 7 in second-quantization as follows:

$$\hat{H}_{PS} = \sum_{\mu\nu} \overline{T}^{nuc}_{\mu\nu} a^\dagger_\mu a_\nu + \hat{H}_{el} \tag{23}$$

$$\overline{T}^{nuc}_{\mu\nu} = \sum_{\lambda\sigma} S^{-1}_{\mu\lambda} T^{nuc}_{\lambda\sigma} S^{-1}_{\sigma\nu} \tag{24}$$

$$T^{nuc}_{\mu\nu} \overset{?}{=} \sum_{A\lambda\sigma} \frac{1}{2M_A} (\mathbf{P}_A\delta_{\mu\lambda} - i\hbar\tilde{\Gamma}^{A}_{\mu\lambda}) S_{\lambda\sigma} (\mathbf{P}_A\delta_{\sigma\nu} - i\hbar\tilde{\Gamma}^{A}_{\sigma\nu}) \tag{25}$$

where we fix $\tilde{\mathbf{\Gamma}}$ to be the solution to

$$\frac{1}{2} \sum_\lambda \tilde{\mathbf{\Gamma}}^{A}_{\mu\lambda} S_{\lambda\nu} + S_{\mu\lambda} \tilde{\mathbf{\Gamma}}^{A}_{\lambda\nu} = \mathbf{\Gamma}^{A}_{\boldsymbol{\mu\nu}} \tag{26}$$

Note that, just as in eq 9, eq 25 expresses the kinetic energy in product form and posits that the function $\boldsymbol{P}_A - \tilde{\mathbf{\Gamma}}^{A}_{\mu\lambda}$ represents a kinetic momentum operator; intuitively, the $\tilde{\mathbf{\Gamma}}^{A}_{\mu\lambda}$ captures how electrons are dragged by a nucleus whenever that nucleus moves—because each nucleus carries a basis function along for the ride. Unfortunately, however, this operator only makes sense for a one electron problem. After all, if one inserts eq 25 into eq 24 and then into eq 23, one will find that $\hat{\boldsymbol{H}}_{PS}$ contains a term proportional to $\sum_A \frac{\mathbf{P}_A \cdot \mathbf{P}_A}{2M_A} \sum_{\mu\nu} S^{-1}_{\mu\nu} a^\dagger_\mu a_\nu$, and it is easy to show that for any wave function, $\langle S^{-1}_{\mu\nu}\, a^\dagger_\mu\, a_\nu \rangle = N_e$, where N_e is the number of electrons. Thus, eqs 23-25 cannot be a meaningful Hamiltonian for a many-electron system where $N_e \neq 1$. Nevertheless, we can now identify one plausible many-body Hamiltonian that (i) reduces to product form for the case of a single electron, (ii) maintains angular and linear momentum conservation and (iii) has a positive definite kinetic energy (See Appendix E). Namely, we can make the ansatz that a reasonable semiclassical phase-space electronic Hamiltonian is

$$\hat{H}_{PS} = \hat{H}_{el} + \frac{\mathbf{P}_A \cdot \mathbf{P}_A}{2M_A} - i\hbar \sum_{A\alpha\mu\nu} \frac{P_{A\alpha} \cdot \overline{\Gamma}^{A\alpha}_{\mu\nu}}{M_A} a^\dagger_\mu a_\nu + \sum_{A\alpha\mu\nu} \frac{\overline{\zeta^{A\alpha}_{\mu\nu}}}{M_A} a^\dagger_\mu a_\nu \tag{27}$$

$$\overline{\mathbf{\Gamma}}^{A}_{\mu\nu} = \sum_{\lambda\sigma} S^{-1}_{\mu\lambda} \mathbf{\Gamma}^{A}_{\lambda\sigma} S^{-1}_{\sigma\nu} \tag{28}$$

$$\overline{\zeta^{A\alpha}_{\mu\nu}} = -\hbar^2 \sum_{\lambda\sigma\kappa\eta} S^{-1}_{\mu\lambda} \tilde{\Gamma}^{A\alpha}_{\lambda\kappa} S_{\kappa\eta} \tilde{\Gamma}^{A\alpha}_{\eta\sigma} S^{-1}_{\sigma\nu} \tag{29}$$

where $\tilde{\mathbf{\Gamma}}_{\mu\nu}$ is defined in eq 26 and we show how to solve this equation in In Appendix E. Note that our explicit form for $\mathbf{\Gamma}$ is defined in Appendix F (following ref 35). Equations 27−29 represent the final form of our proposed phase-space electronic Hamiltonian. Just as in eq 22 above, one can easily write down the final energy for this Hamiltonian:

$$E_{\mathrm{PS}}(\mathbf{R},\,\mathbf{P}) = \sum_{\mathrm{A}\alpha} \frac{P_{\mathrm{A}\alpha}^2}{2M_{\mathrm{A}}} + \sum_{\mu\nu} D_{\nu\mu}\left(h_{\mu\nu} - i\hbar \sum_{\mathrm{A}\alpha} \frac{P_{\mathrm{A}\alpha}\Gamma_{\mu\nu}^{\mathrm{A}\alpha}}{M_{\mathrm{A}}} - \sum_{\mathrm{A}\alpha\lambda\sigma} \hbar^2 \frac{\tilde{\Gamma}_{\mu\sigma}^{\mathrm{A}\alpha} S_{\sigma\lambda} \tilde{\Gamma}_{\lambda\nu}^{\mathrm{A}\alpha}}{2M_{\mathrm{A}}}\right) + \sum_{\mu\nu\lambda\sigma} G_{\nu\mu\sigma\lambda}\pi_{\mu\nu\lambda\sigma} \tag{30}$$

Note that, according to ref 35, $\mathbf{\Gamma}$ acts like an effective vector potential (which generates an effective magnetic field), so that the canonical momentum ($\boldsymbol{P}$) is not equal to the kinetic momentum except at ($\mathbf{\Pi} = \boldsymbol{P} = \mathbf{0}$), and even then, the derivatives $\frac{\partial}{\partial \Pi_{\mathrm{A}\alpha}} \neq \frac{\partial}{\partial P_{\mathrm{A}\alpha}}$. In particular,

$$\dot{X}_{\mathrm{A}\alpha} = \frac{\partial E_{\mathrm{PS}}}{\partial P_{\mathrm{A}\alpha}} = \frac{P_{\mathrm{A}\alpha}}{M_{\mathrm{A}}} - i\hbar \mathrm{Tr}\left(\frac{\Gamma^{\mathrm{A}\alpha} D}{M_{\mathrm{A}}}\right) \neq \frac{P_{\mathrm{A}\alpha}}{M_{\mathrm{A}}} \tag{31}$$

2.4. The Harmonic Approximation and Normal Modes for Phase-Space Electronic Hamiltonians.

The basis of eigenvectors from the phase-space electronic Hamiltonian in eq 28,

$$\hat{H}_{\mathrm{PS}}(\mathbf{R},\,\mathbf{P})|\Phi_J^{\mathrm{PS}}\rangle = E_J^{\mathrm{PS}}(\mathbf{R},\,\mathbf{P})|\Phi_J^{\mathrm{PS}}\rangle \tag{32}$$

gives a new basis for expansion of the total nuclear-electronic wave function,

$$|\Psi_{\mathrm{tot}}(t)\rangle = \int \mathrm{d}\mathbf{R} \int \mathrm{d}\mathbf{P} \sum_J \Omega_J(\mathbf{R},\,\mathbf{P},\,t)|\mathbf{R},\,\mathbf{P}\rangle|\Phi_J^{\mathrm{PS}};\,\mathbf{R},\,\mathbf{P}\rangle \tag{33}$$

where $|\boldsymbol{R},\boldsymbol{P}\rangle$ is a coherent nuclear state. Evaluating $\Omega_J(\boldsymbol{R},\,\boldsymbol{P},\,t)$ and diagonalizing a quantum Hamiltonian would appear to be difficult both numerically and conceptually given the fact that the coherent basis $\{|\boldsymbol{R},\boldsymbol{P}\rangle\}$ is overcomplete. That being said, to the zeroth order, however, the first and most important step is usually to make a one-state approximation and extract vibrational energies. And in that vein, one usually begins by expanding the potential surfaces to second order and generating normal modes and vibrational frequencies.

2.4.1. Approach to Normal Modes in a Born–Oppenheimer Representation.

Before addressing how to construct phase-space normal modes, let us review for the usual notation for a Born–Oppenheimer expansion. One defines $V(\boldsymbol{R}) = E_G(\boldsymbol{R})$ (the lowest eigenvalue of $\hat{\boldsymbol{H}}_{\mathrm{el}}$ in eq 4) and expands to second order in displacements from equilibrium:

$$V(\mathbf{R}) = V(\mathbf{R}_{\mathrm{eq}}) + \frac{1}{2} \sum_{\mathrm{A}\alpha,\mathrm{B}\beta} K_{\mathrm{A}\alpha,\mathrm{B}\beta}(R_{\mathrm{A}\alpha} - R_{\mathrm{A}\alpha}^{\mathrm{eq}})(R_{\mathrm{B}\beta} - R_{\mathrm{B}\beta}^{\mathrm{eq}}) \tag{34}$$

If now one regards the quantities $\{R_{\mathrm{A}\alpha}\}$ as operators (rather than scalars), i.e., one quantizes these operators, the vibrational Hamiltonian is then defined as

$$\hat{H}_{\mathrm{vib}} = \frac{1}{2M}\hat{\mathbf{P}}\cdot\hat{\mathbf{P}} + V(\hat{\mathbf{R}}) \tag{35}$$

$$= \sum_{\mathrm{A}\alpha} \frac{1}{2M_{\mathrm{A}}}\hat{P}_{\mathrm{A}\alpha}^2 + V(\mathbf{R}_{\mathrm{eq}}) + \frac{1}{2} \sum_{\mathrm{A}\alpha,\mathrm{B}\beta} K_{\mathrm{A}\alpha,\mathrm{B}\beta}(\hat{R}_{\mathrm{A}\alpha} - R_{\mathrm{A}\alpha}^{\mathrm{eq}})(\hat{R}_{\mathrm{B}\beta} - R_{\mathrm{B}\beta}^{\mathrm{eq}}) \tag{36}$$

where $K_{\mathrm{A}\alpha,\mathrm{B}\beta} = \frac{\partial^2 V}{\partial R_{\mathrm{A}\alpha}\partial R_{\mathrm{B}\beta}}$ (i.e., $\mathbf{K}^{\mathrm{BO}} = \frac{\partial^2 V}{\partial \mathbf{R}\partial \mathbf{R}}$ in matrix form) is the Hessian matrix. Normal modes are generated by shifting to relative coordinates (setting $\boldsymbol{R}^{\mathrm{eq}} = 0$), ignoring the equilibrium energy (C-number), and converting to mass-weighted coordinates given by

$$\hat{\mathbf{R}} = \hat{\mathbf{R}}'' M_{\mathrm{BO}}^{-1/2} \tag{37}$$

$$\hat{\mathbf{P}} = \hat{\mathbf{P}}'' M_{\mathrm{BO}}^{1/2} \tag{38}$$

where we define M_{BO} as the diagonal matrix of nuclear masses, which eliminates the masses in the kinetic energy. This leaves

$$\hat{H}_{\mathrm{vib}} = \frac{1}{2}\hat{\mathbf{P}}''^{\dagger}\hat{\mathbf{P}}'' + \frac{1}{2}\hat{\mathbf{R}}''^{\dagger}\mathbf{K}''\hat{\mathbf{R}}'' \tag{39}$$

where $\boldsymbol{K}'' = M_{\mathrm{BO}}^{-1/2}\boldsymbol{K}M_{\mathrm{BO}}^{-1/2}$. Finally, one diagonalizes the resulting Hamiltonian $\boldsymbol{K}''$ and the result is a series of uncoupled mass-weighted normal-mode oscillators.

2.4.2. Approach to Normal Modes in a Phase-Space Representation.

The procedure above can be largely replicated in a phase-space picture. One expands the lowest eigenvalue of our phase-space electronic Hamiltonian $E_{\mathrm{PS}}(\boldsymbol{R},\boldsymbol{P})$ in eq 30 to second order (in both $\boldsymbol{R}$ and $\boldsymbol{P}$), requantizes them (in the spirit of a Weyl transform), and then one finds:

$$\hat{H}_{\mathrm{vib}} = E_{\mathrm{PS}}(\mathbf{R}^{\mathrm{eq}},\,\mathbf{P}^{\mathrm{eq}}) + \frac{1}{2} \sum_{\mathrm{A}\alpha,\mathrm{B}\beta} W_{\mathrm{A}\alpha,\mathrm{B}\beta}(\hat{P}_{\mathrm{A}\alpha} - P_{\mathrm{A}\alpha}^{\mathrm{eq}})(\hat{P}_{\mathrm{B}\beta} - P_{\mathrm{B}\beta}^{\mathrm{eq}}) + \frac{1}{2} \sum_{\mathrm{A}\alpha,\mathrm{B}\beta} K_{\mathrm{A}\alpha,\mathrm{B}\beta}(\hat{R}_{\mathrm{A}\alpha} - R_{\mathrm{A}\alpha}^{\mathrm{eq}})(\hat{R}_{\mathrm{B}\beta} - R_{\mathrm{B}\beta}^{\mathrm{eq}}) + \frac{1}{4} \sum_{\mathrm{A}\alpha,\mathrm{B}\beta} Y_{\mathrm{A}\alpha,\mathrm{B}\beta}[(\hat{R}_{\mathrm{A}\alpha} - R_{\mathrm{A}\alpha}^{\mathrm{eq}})(\hat{P}_{\mathrm{B}\beta} - P_{\mathrm{B}\beta}^{\mathrm{eq}}) + (\hat{P}_{\mathrm{A}\alpha} - P_{\mathrm{A}\alpha}^{\mathrm{eq}})(\hat{R}_{\mathrm{B}\beta} - R_{\mathrm{B}\beta}^{\mathrm{eq}}) + (\hat{P}_{\mathrm{B}\beta} - P_{\mathrm{B}\beta}^{\mathrm{eq}})(\hat{R}_{\mathrm{A}\alpha} - R_{\mathrm{A}\alpha}^{\mathrm{eq}}) + (\hat{R}_{\mathrm{B}\beta} - R_{\mathrm{B}\beta}^{\mathrm{eq}})(\hat{P}_{\mathrm{A}\alpha} - P_{\mathrm{A}\alpha}^{\mathrm{eq}})] \tag{40}$$

where $W_{\mathrm{A}\alpha,\mathrm{B}\beta} = \left(\frac{\partial^2 E_{\mathrm{PS}}}{\partial P_{\mathrm{A}\alpha}\partial P_{\mathrm{B}\beta}}\right)_{\mathrm{eq}}$, $K_{\mathrm{A}\alpha,\mathrm{B}\beta} = \left(\frac{\partial^2 E_{\mathrm{PS}}}{\partial R_{\mathrm{A}\alpha}\partial R_{\mathrm{B}\beta}}\right)_{\mathrm{eq}}$, and $Y_{\mathrm{A}\alpha,\mathrm{B}\beta} = \left(\frac{\partial^2 E_{\mathrm{PS}}}{\partial P_{\mathrm{A}\alpha}\partial R_{\mathrm{B}\beta}}\right)_{\mathrm{eq}}$. See Appendix C for explicit forms of $W_{\mathrm{A}\alpha,\mathrm{B}\beta}$, $K_{\mathrm{A}\alpha,\mathrm{B}\beta}$, and $Y_{\mathrm{A}\alpha,\mathrm{B}\beta}$. Note that, in the results presented below, we do not invoke any spin degrees of freedom, which implies that $\boldsymbol{Y} = 0$ and $\boldsymbol{P}_{\mathrm{eq}} = 0$ and simplifies the diagonalization procedure (see Appendix C). Shifting to relative positional coordinates and ignoring equilibrium energy, the total vibrational Hamiltonian is of the form

$$\hat{H}_{\mathrm{vib}} = \frac{1}{2}\hat{\mathbf{P}}^{\dagger}\mathbf{W}\hat{\mathbf{P}} + \frac{1}{2}\hat{\mathbf{R}}^{\dagger}\mathbf{K}\hat{\mathbf{R}} \tag{41}$$

Unfortunately, unlike in the BO representation, $\boldsymbol{W}$ is not diagonal by construction. Thus, in order to find the normal modes which diagonalize our separable phase-space electronic Hamiltonian, we first need to find the unitary transformation which diagonalizes $\boldsymbol{W} = U\ \Delta U^{\dagger}$(where $\Delta\ \approx M_{\mathrm{BO}}^{-1}$ for small perturbations to the uncoupled momentum Hessian). Taking the coordinate transformation $\boldsymbol{R} = U\ \boldsymbol{R}'$, $\boldsymbol{P} = U\ \boldsymbol{P}'$, eq 41 can then be written as

$$\hat{H}_{\mathrm{vib}} = \frac{1}{2}\hat{\mathbf{P}}'^{\dagger}\Delta\hat{\mathbf{P}}' + \frac{1}{2}\hat{\mathbf{R}}'^{\dagger}U^{\dagger}\mathbf{K}U\hat{\mathbf{R}}' \tag{42}$$

eq 42 is diagonal in momenta but with new effective masses. Thus, if we again change to mass-weighted coordinates $\boldsymbol{R}' = \Delta^{1/2}\boldsymbol{R}''$, $\boldsymbol{P}' = \Delta^{-1/2}\boldsymbol{P}''$, we find

$$\hat{H}_{\mathrm{vib}} = \frac{1}{2}\hat{\mathbf{P}}''^{\dagger}\hat{\mathbf{P}}'' + \frac{1}{2}\hat{\mathbf{R}}''^{\dagger}\Delta^{1/2}U^{\dagger}\mathbf{K}U\Delta^{1/2}\hat{\mathbf{R}}'' \tag{43}$$

$$= \frac{1}{2}\hat{\mathbf{P}}''^{\dagger}\hat{\mathbf{P}}'' + \frac{1}{2}\hat{\mathbf{R}}''^{\dagger}\mathbf{K}''\hat{\mathbf{R}}'' \tag{44}$$

which is of the same form as the standard quadratic expansion in the BO representation (eq 39). If $\boldsymbol{k}''$ are the eigenvectors of $\boldsymbol{K}''$, the nuclear normal modes in our original Cartesian coordinates are then simply

$$\mathbf{k} = U\Delta^{1/2}\mathbf{k}'' \tag{45}$$

After diagonalization, we write the final form for the Hamiltonian in normal coordinates as the sum of independent harmonic oscillators:

$$\hat{H}_{\mathrm{vib}} = \frac{1}{2}\hat{\mathcal{P}}_k^2 + \sum_k \frac{1}{2}w_k^2\hat{Q}_k^2 \tag{46}$$

2.5. Rotatory Strength in Phase-Space Framework.

If the interaction between an electromagnetic field with a molecular system is given by $\hat{H}_{\mathrm{int}} = -\hat{\boldsymbol{\mu}}\cdot\mathbf{E}_{\mathrm{ext}} - \hat{\boldsymbol{m}}\cdot\mathbf{B}_{\mathrm{ext}}$, then when averaged over all incoming light directions, the differential absorbance to circularly polarized light of chiral vibrations is given by the rotatory strength:[58]

$$\mathcal{R} = Im[\langle\Psi_{Gg}|\hat{m}|\Psi_{Ge}\rangle\cdot\langle\Psi_{Ge}|\hat{\boldsymbol{\mu}}|\Psi_{Gg}\rangle] \tag{47}$$

The magnetic moment $\boldsymbol{m}$ and electric moment $\boldsymbol{\mu}$ each contains an electronic component and a nuclear component. Ignoring spin contributions, these operators are given as

$$\hat{\boldsymbol{m}}^e = \frac{-e}{2m_e}\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}} = \frac{-e}{2m_e}\hat{\boldsymbol{L}}^e \tag{48}$$

$$\hat{\boldsymbol{m}}^n = \sum_{\mathrm{A}}\frac{Z_{\mathrm{A}}e}{M_{\mathrm{A}}2}\hat{\mathbf{R}}_{\mathrm{A}}\times\hat{\mathbf{P}}_{\mathrm{A}} \tag{49}$$

$$\hat{\boldsymbol{\mu}}^e = -e\hat{\boldsymbol{r}} \tag{50}$$

$$\hat{\boldsymbol{\mu}}^n = \sum_{\mathrm{A}}Z_{\mathrm{A}}e\hat{\mathbf{R}}_{\mathrm{A}} \tag{51}$$

Note that in eqs 48–51, we use the standard $\boldsymbol{r}$, $\boldsymbol{p}$, $\boldsymbol{R}$, $\boldsymbol{P}$ coordinates to express the magnetic and electric moments. These expressions ignore the fact that formally these operators are dressed under a diabatic-to-adiabatic transformation and, e.g., convert a canonical momentum $\boldsymbol{P}$ to a kinetic momentum $\boldsymbol{\Pi}$. Nevertheless, one expects these dressings to be small and so they are ignored at this level of treatment. For instance, following eq 31, it follows that

$$\left(\frac{\partial\mathbf{\Pi}}{\partial\mathbf{P}}\right)_R = 1 - i\hbar\mathrm{Tr}(D^{[P]}\cdot\mathbf{\Gamma})_R \approx 1 \tag{52}$$

where the subscript R indicates that nuclear coordinates are kept constant, $D^{[P]}$ is the momentum derivative of the density matrix, and we assume Γ is small. With this caveat in mind, let us evaluate $\boldsymbol{\mu}$. For a transition between product nuclear-electronic wave functions (in the spirit of the BO approximation), we can evaluate

$$\begin{aligned}\langle\Psi_{Gg}|\hat{\boldsymbol{\mu}}|\Psi_{Ge}\rangle &= \langle\Omega_{Gg}|\otimes\langle\Phi_G|\hat{\boldsymbol{\mu}}^e|\Phi_G\rangle\otimes|\Omega_{Ge}\rangle + \langle\Omega_{Gg}|\hat{\boldsymbol{\mu}}^n|\Omega_{Ge}\rangle\\ &\equiv\langle\Omega_{Gg}|\hat{\boldsymbol{\mu}}_G|\Omega_{Ge}\rangle\end{aligned} \tag{53}$$

If one neglects the dependence of $\boldsymbol{\mu}_G$ on $\boldsymbol{R}$ (and evaluates $\boldsymbol{\mu}_G$ at $\boldsymbol{R}_{\mathrm{eq}}$), then eq 53 vanishes by the orthogonality of Ω_{Gg} and Ω_{Ge}. In order to obtain a nonzero rotatory strength, one must expand in nuclear coordinates around $\boldsymbol{R} = \boldsymbol{R}_{\mathrm{eq}}$. Doing so and invoking the harmonic approximation yields the following expression for the transition electric dipole moment:

$$\begin{aligned}\langle\Omega_{Ge}|\langle\Phi_G|\hat{\boldsymbol{\mu}}|\Phi_G\rangle|\Omega_{Gg}\rangle &= \langle\Omega_{Ge}|(\boldsymbol{\mu}_G)_{\mathrm{eq}} + \sum_{\mathrm{A}\alpha}\left(\frac{\partial\boldsymbol{\mu}_G}{\partial R_{\mathrm{A}\alpha}}\right)_{\mathrm{eq}}\cdot(\hat{R}_{\mathrm{A}\alpha} - R_{\mathrm{A}\alpha}^{\mathrm{eq}})|\Omega_{Gg}\rangle\\ &= \sum_{\mathrm{A}\alpha}\left(\frac{\partial\boldsymbol{\mu}_G}{\partial R_{\mathrm{A}\alpha}}\right)_{\mathrm{eq}}\cdot\langle\Omega_{Ge}|(\hat{R}_{\mathrm{A}\alpha} - R_{\mathrm{A}\alpha}^{\mathrm{eq}})|\Omega_{Gg}\rangle\\ &= \sum_k\sum_{\mathrm{A}\alpha}\left(\frac{\partial\boldsymbol{\mu}_G}{\partial R_{\mathrm{A}\alpha}}\right)_{\mathrm{eq}}\left(\frac{\hbar}{2M_{\mathrm{A}}\omega_k}\right)^{1/2}\mathcal{S}_{\mathrm{A}\alpha,k}\end{aligned} \tag{54}$$

Here, the element $\mathcal{S}_{\mathrm{A}\alpha,k}$ quantifies the displacement of nucleus A in direction α for the kth vibrational mode and is defined as

$$\mathcal{S}_{\mathrm{A}\alpha,k} = \frac{\partial R_{\mathrm{A}\alpha}}{\partial Q_k} = \frac{\partial\dot{R}_{\mathrm{A}\alpha}}{\partial\mathcal{P}_k} = \frac{1}{M_{\mathrm{A}}}\frac{\partial P_{\mathrm{A}\alpha}}{\partial\mathcal{P}_k} \tag{55}$$

where Q_k and $\mathcal{P}_k$ are, respectively, the mass-weighted position modes and mass-weighted momentum modes from eq 46. This completes our treatment of $\frac{\partial\boldsymbol{\mu}}{\partial\mathbf{R}}$.

Next, we turn to $\langle\Psi_{Gg}|\hat{m}|\Psi_{Ge}\rangle$. At the equilibrium geometry ($\boldsymbol{R} = \boldsymbol{R}_{\mathrm{eq}}$) and equilibrium momentum ($\boldsymbol{P} = 0$), $\langle\Phi_G|\hat{m}^e|\Phi_G\rangle|_{\mathbf{R}_{\mathrm{eq}},0} = 0$, since $\hat{m}^e$ is a purely imaginary Hermitian operator and Φ_G can be chosen real for a time-reversible ground state. Furthermore, $\langle\hat{m}^n\rangle$ also clearly vanishes if $\boldsymbol{P} = 0$. We conclude that $\boldsymbol{m}$ vanishes for all nuclear geometries unless $\boldsymbol{P} \neq 0$, and thus expand $\boldsymbol{m}$ in the canonical momentum $\boldsymbol{P}$:

$$\begin{aligned}\langle\Omega_{Gg}|\langle\Phi_G|\hat{m}|\Phi_G\rangle|\Omega_{Ge}\rangle &= \langle\Omega_{Gg}|(m_G)_{\mathrm{eq}} + \sum_{\mathrm{A}\alpha}\left(\frac{\partial m_G}{\partial P_{\mathrm{A}\alpha}}\right)_{\mathrm{eq}}\cdot\hat{P}_{\mathrm{A}\alpha}|\Omega_{Ge}\rangle\\ &= \sum_{\mathrm{A}\alpha}\left(\frac{\partial m_G}{\partial P_{\mathrm{A}\alpha}}\right)_{\mathrm{eq}}\cdot\langle\Omega_{Gg}|\hat{P}_{\mathrm{A}\alpha}|\Omega_{Ge}\rangle\\ &= \sum_k\sum_{\mathrm{A}\alpha}\left(\frac{\partial m_G}{\partial P_{\mathrm{A}\alpha}}\right)_{\mathrm{eq}}M_{\mathrm{A}}\mathcal{S}_{\mathrm{A}\alpha,k}i\left(\frac{\hbar M_{\mathrm{A}}\omega_k}{2}\right)^{1/2}\end{aligned} \tag{56}$$

Plugging eqs 54 and 56 into eq 47, we find the rotational strength for the kth mode to be

$$\mathcal{R}_k = \sum_{A\alpha, A\alpha'} \frac{\hbar M_A}{2} S_{A\alpha,k} S_{A'\alpha',k} \left(\frac{\partial \boldsymbol{m}_G}{\partial P_{A\alpha}}\right)_{\mathrm{eq}} \cdot \left(\frac{\partial \boldsymbol{\mu}_G}{\partial R_{A'\alpha'}}\right)_{\mathrm{eq}} \tag{57}$$

2.6. Evaluating m and μ within Generalized Hartree–Fock Theory. Phase-space approaches break the time reversibility of the electronic Hamiltonian and therefore necessitate complex wave functions whenever the nuclear momentum is nonzero. In that vein, the simplest applicable electronic structure method is generalized Hartree–Fock (GHF) theory, where the ansatz of the wave function is a Slater determinant where the orbitals are allowed to be complex-valued. (In the present paper, we ignore all spin-couplings, so that the orbitals do still keep s_z as a good quantum number.) Moreover, as discussed in Section 2.2 above, for nondegenerate electronic wave functions without fine structure, $\boldsymbol{P}_{\mathrm{eq}} = 0$, so that the zeroth-order magnetic moment remains zero. With this information, we can evaluate $\boldsymbol{m}$ and $\boldsymbol{\mu}$ within GHF theory.

Inserting the definition for $\hat{\boldsymbol{m}}^e$ given in eq 48 allows us to directly calculate $\frac{\partial \boldsymbol{m}}{\partial \mathbf{P}}$ as (dropping the "G" for notational simplicity):

$$\begin{aligned} \frac{\partial m_\beta}{\partial P_{A\alpha}} &= \frac{\partial}{\partial P_{A\alpha}} (\langle \Phi_G | \hat{m}^e_\beta | \Phi_G \rangle + m^n_\beta) \\ &= \frac{-e}{2m_e} \frac{\partial}{\partial P_{A\alpha}} \langle \Phi_G | \hat{L}^e_\beta | \Phi_G \rangle + \sum_\gamma \frac{Z_A e}{2M_A} \epsilon_{\alpha\beta\gamma} R_{A\gamma} \\ &= \frac{-e}{2m_e} \sum_{\mu,\nu} \frac{\partial D_{\mu\nu}}{\partial P_{A\alpha}} \langle \chi_\mu | \sum_{\gamma\delta} \epsilon_{\beta\gamma\delta} \hat{r}_\gamma \hat{p}_\delta | \chi_\nu \rangle + \sum_\gamma \frac{Z_A e}{2M_A} \epsilon_{\alpha\beta\gamma} R_{A\gamma} \end{aligned} \tag{58}$$

The components of $\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{R}}$ are similarly given as

$$\begin{aligned} \frac{\partial \mu_\beta}{\partial R_{A\alpha}} &= \frac{\partial}{\partial R_{A\alpha}} (\langle \Phi_G | \hat{\mu}^e_\beta | \Phi_G \rangle + \mu^n_\beta) \\ &= -e \frac{\partial}{\partial R_{A\alpha}} \langle \Phi_G | \hat{r}_\beta | \Phi_G \rangle + e Z_A \delta_{\beta\alpha} \\ &= -e \left(\sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial R_{A\alpha}} \langle \chi_\mu | \hat{r}_\beta | \chi_\nu \rangle + D_{\mu\nu} \frac{\partial}{\partial R_{A\alpha}} \langle \chi_\mu | \hat{r}_\beta | \chi_\nu \rangle \right) + e Z_A \delta_{\beta\alpha} \end{aligned} \tag{59}$$

Finally, components of $\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{P}}$ are given as

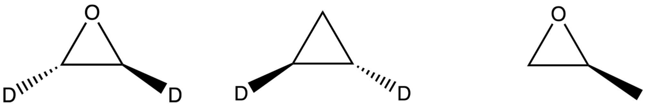
$$\begin{aligned} \frac{\partial \mu_\beta}{\partial P_{A\alpha}} &= \frac{\partial}{\partial P_{A\alpha}} (\langle \Phi_G | \hat{\mu}^e_\beta | \Phi_G \rangle + \mu^n_\beta) \\ &= -e \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial P_{A\alpha}} \langle \chi_\mu | \hat{r}_\beta | \chi_\nu \rangle \end{aligned} \tag{60}$$

Note that at $\boldsymbol{P}_{\mathrm{eq}} = 0$, $\frac{\partial D_{\mu\nu}}{\partial P_{A\alpha}}$ is imaginary Hermitian, whereas the matrix $r_{\beta,\mu\nu}$ is real symmetric, and thus $\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{P}} = 0$. Expressions for calculating $\frac{\partial D_{\mu\nu}}{\partial R_{A\alpha}}$ and $\frac{\partial D_{\mu\nu}}{\partial P_{A\alpha}}$ through a coupled-perturbed Hartree–Fock (CPHF) phase-space approach are given in Appendix B.

3. NUMERICAL RESULTS

The theory above has been implemented within a developmental version of the Q-Chem electronic structure package.[59] To benchmark the rotational strength expression from eq 57 above, we have modeled a set of small rigid chiral molecules: S-d_2-oxirane (Chart 1a), R-d_2-cyclopropane (Chart 1b), and S-propylene-oxide (Charta 1c). These molecules have been previously characterized quite sensitively by Nafie and others,[60−62] so that we can directly compare our results vs experimental data (with the caveat that the latter are not in the gas phase). As far as the gauge origin in concerned, all of our calculations are run with a distributed origin gauge, whereas the MFP calculations are run with a common origin and GIAOs. For more details, see Appendix A.

Chart 1



(a) S-d_2-oxirane (b) R-d_2-cyclopropane (c) S-propylene-oxide

3.1. VCD Spectra. In Figures 1−3, we plot $\mathcal{R}$ as calculated for the normal modes of each molecule vs an MFP calculation

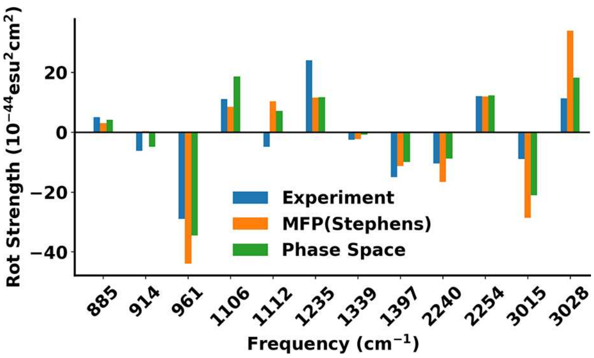


Figure 1. Experimental[61] rotational strength of S-d_2-oxirane vs theoretical results using either Γ coupling or MFP. Experimental conditions reported in Table 3. All theoretical calculations are in vacuum (GHF/aug-cc-pvqz). All frequencies listed on the x-axis are the experimental values. For this problem, phase-space methods would appear to outperform MFP methods.

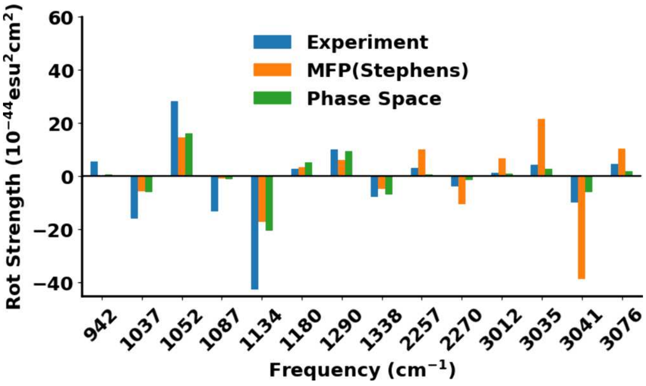


Figure 2. Experimental[60] rotational strength of R-d_2-cyclopropane vs theoretical results using either Γ coupling or MFP. Experimental conditions reported in Table 4. All theoretical calculations are in vacuum (GHF/aug-cc-pvqz). All frequencies listed on the x-axis are the experimental values. For this problem, phase-space methods would appear to outperform MFP methods.

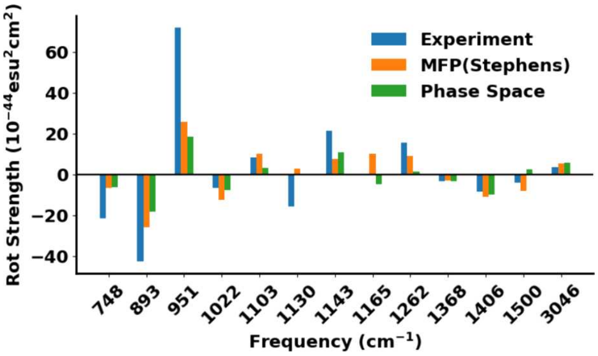


Figure 3. Experimental[62] rotational strength of S-propylene-oxide vs theoretical results using either Γ coupling or MFP. Experimental conditions reported in Table 5. All theoretical calculations are in vacuum (GHF/aug-cc-pvqz). All frequencies listed on the x-axis are the experimental values. For this problem, phase-space methods would appear to underperform MFP methods.

and vs experiment. Note that these data were gathered using the phase-space electronic Hamiltonian in eq 28 (which includes a second-derivative term). Although not shown, if one were to use the Hamiltonian in eq 22 (without a second-derivative coupling term), the answers would be terrible—mostly because the normal modes are nonphysical (and very different from the standard normal modes). As we highlighted above, it seems that in order to retrieve meaningful normal modes with a phase-space electronic Hamiltonian, the kinetic energy must be positive (which is not true without the second derivative). A visualization of a phase-space normal mode for the molecule **1a** (relative to a standard normal mode) is given in Figure 4.

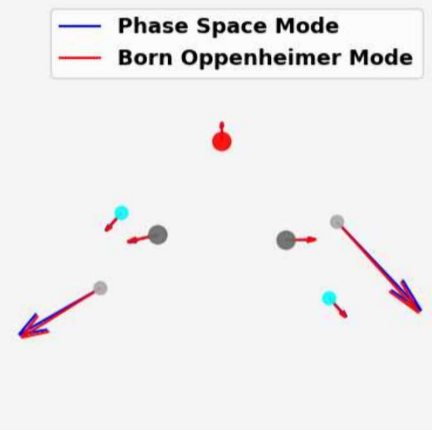


Figure 4. Oxirane 3256 cm^{-1} H Sym stretch mode (3291 cm^{-1} BO), according to both a BO and phase-space Hessian (where we plot the spatial components of the phase-space mode).

Let us now turn to the rotatory strengths. As shown in Figures 1−3, both our data and the MFP data recover the experimental data reasonably well, although we submit that phase-space methods perform better for Figures 1 and 2 (especially for large frequencies). This finding is interesting insofar as our method only includes the nondiverging portion of the electronic momentum coupling (as compared with MFP). Neither MFP nor our phase approach recovers the exact experimental data perfectly, for which one can propose a slew of explanations. First, on the experimental side, the data are acquired in solution, and furthermore some of the data arise between closely spaced vibrations (in the presence of mode degeneracy, ascertaining the strength of a VCD signal for a particular mode can be difficult). Second, on the theoretical side, we note that we have used a GHF calculation and entirely ignored direct electron−electron correlation.[63] We have also sampled only a single nuclear geometry per molecule, and we have ignored all anharmonic effects.[63−66]

Notwithstanding all of these limitations, the rough accuracy of the data presented in Figure 1−3 highlights the fact that even a crude phase-space approach can recover some very sensitive optical signals. For the raw data behind these graphs, see the tables in Appendix G.

Before concluding this paper, a few words are appropriate regarding the non-BO part of the W term in eq 40. Note that the concept of effective masses is very old and has been standardized in just about all spectroscopy books. Here, however, we have found that, with a phase-space electronic Hamiltonian, we must replace the diagonal inverse mass tensor with a nondiagonal "inverse mass" tensor (which must be diagonalized in order to recover spectra, see Section 2.4). One can ask: For such a non-diagonal tensor, what is the meaning of the on-diagonal elements? How close do the values resemble the inverse masses of the nuclei?

To that end, in Tables 1 and 2, we list both the inverse of the eigenvalues of W and the inverse of the diagonal elements

Table 1. Inverses of the Eigenvalues of W in eq 40[a]

Inverses of the Eigenvalues of W (amu)		
S-d_2-oxirane	R-d_2-cyclopropane	S-propylene-oxide
1.0309	2.0338	16.041
1.0307	2.0335	16.0249
1.0164	2.0224	16.0151
1.0166	2.022	12.0318
1.0195	2.0246	12.0534
1.0199	2.0246	12.0344
2.0369	1.0281	12.0366
2.0367	1.028	12.0503
2.0226	1.0274	12.0488
2.0228	1.027	12.0425
2.0257	1.013	12.0442
2.0261	1.014	12.0434
16.0382	1.0169	1.0109
16.0237	1.0193	1.0302
16.013	1.0189	1.0297
12.0599	1.0181	1.0292
12.0415	1.0186	1.0285
12.0528	1.0184	1.0132
12.045	12.0266	1.0137
12.048	12.0265	1.0264
12.0466	12.0315	1.026
	12.0355	1.0155
	12.0462	1.0166
	12.042	1.0216
	12.042	1.021
	12.0444	1.0207
	12.0444	1.0203
		1.0191
		1.0193
		1.0193

[a] These data represent one estimate of a dressed "effective mass".

Table 2. Inverse Diagonal Elements of W in eq 40[a]

Inverse Diagonal Elements of W					
S-d_2-oxirane		R-d_2-cyclopropane		S-propylene-oxide	
C	12.0470	H	1.0214	C	12.0411
C	12.0492	H	1.0171	C	12.0369
C	12.0497	H	1.0233	C	12.0409
C	12.0470	C	12.0369	C	12.0470
C	12.0492	C	12.0372	C	12.0483
C	12.0497	C	12.0382	C	12.0460
H	1.0217	H	1.0182	H	1.0249
H	1.0263	H	1.0203	H	1.0189
H	1.0189	H	1.0233	H	1.0215
H	1.0217	H	1.0182	H	1.0189
H	1.0263	H	1.0203	H	1.0229
H	1.0189	H	1.0233	H	1.0252
O	16.0235	C	12.0374	H	1.0202
O	16.0129	C	12.0367	H	1.0194
O	16.0380	C	12.0382	H	1.0287
D	2.0279	H	1.0182	C	12.0420
D	2.0324	H	1.0203	C	12.0411
D	2.0251	H	1.0233	C	12.0396
D	2.0279	C	12.0369	H	1.0194
D	2.0324	C	12.0372	H	1.0237
D	2.0251	C	12.0382	H	1.0160
		D	2.0244	H	1.0196
		D	2.0265	H	1.0214
		D	2.0295	H	1.0182
		D	2.0276	H	1.0184
		D	2.0233	H	1.0171
		D	2.0295	H	1.0261
				O	16.0250
				O	16.0358
				O	16.0198

[a] These data are another estimate of a dressed "effective mass".

of W. In some sense, these values must correspond to "effective masses" insofar as they have units of mass, but these masses depend on direction and the eigenvectors of W are delocalized. While we cannot easily make any clear conclusions regarding the values of these masses, there is one obvious conclusion from this data: namely, all of the masses are *larger* than the raw masses (usually by 10^{-2} amu). In this regard, experimentalists have pointed out that, for diatomics,[68,69] according to high-resolution spectroscopy, when constructing $\hat{\boldsymbol{H}}_{\text{vib}}$, the masses of nuclei should be set to the mass of the atom (which includes nucleus plus electrons). For a carbon atom with 6 electrons, one would therefore expect an increased carbon mass of 6/1822.9 ≈ 0.003 amu. For the molecules considered hitherto, we predict even larger masses (~10-fold, see Table 1)—although a clear interpretation of these masses is difficult, since we also have off-diagonal components of W and these molecules are not as small as diatomics.

4. DISCUSSION AND CONCLUSIONS

We have presented a phase-space electronic structure approach for calculating VCD signals within GHF theory and compared our results against experiment for three model test cases. Our results demonstrate fairly conclusively that such a phase-space approach—which entirely avoids the BO approximation—is valid and can yield insight into nuclear-electronic coupling that is not available within a BO approximation. Our implementation in a developmental version of QChem[59] is currently quite slow, but, in principle, there is no reason such a phase-space approach should be much slower than standard electronic structure approaches, with the main caveat being the need for complex-valued (rather than real-valued) multiplication.

Interestingly, one finds that our results in Figures 1−3 are comparable with the results of the standard VCD technique, magnetic field perturbation theory. In fact, for Figures 1 and 2, one can easily argue that phase-space approaches outperform MFP theory; though the opposite can be argued for Figure 3. While MFP theory is reviewed below (in Appendix D), it is worth mentioning that MFP is formally a higher-order level calculation than phase-space approaches because the latter accounts only for how electronic orbitals are dragged by nuclei (i.e., the ETF component of the derivative coupling in eq 11), whereas the former includes the entire orbital response (i.e., one calculates $\left|\frac{\partial \Phi_I}{\partial R_{A\alpha}}\right\rangle$, the entire derivative coupling). Thus, one would imagine that MFP theory would match better with Shenvi's phase-space formalism (in eq 9) than would ours.

Thus one must wonder: on the one hand, does the simple phase-space electronic structure Hamiltonian in eq 27 perform so well in Figures 1−3 because the relevant molecules are adiabatically very stable and far from any avoided crossing to another electronic state, but we would not recover such strong results for a more mixed-valence compound? Or, on the other hand, because we argued above that Shenvi's phase-space approach would face limitations near a conical intersection, is it possible that MFP theory will become less accurate near a crossing while our phase-space approach will remain stable? Or perhaps, of course, neither approach will be stable. Ultimately, this thought experiment is a strong reason to run future VCD calculations for more interesting molecules where there is already some ground-state mixing present at equilibrium. This simple thought experiment is one strong reason for us to develop a more rigorous derivation of eq 27 in the future, perhaps using Wigner−Weyl transformations.

Looking forward, in the future we should also confront another key question that inevitably arises in any VCD calculation, namely, the dependence on the chosen origin for the perturbative magnetic field. More details about the choice of origin are given in Appendix A, but the take home-points are as follows:

- On the one hand, the choice of origin should not affect MFP theory in the limit of an infinite (complete) basis. For an incomplete basis, one usually runs MFP calculations with GIAOs (which automatically eliminate origin dependence). Indeed, the MFP data in Figures 1−3 were generated with GIAOs.
- On the other hand, phase-space electronic Hamiltonian calculations using the formalism in Section 2.5 are sensitive to the choice of gauge origin (no matter how big the basis). For this reason, in order to mitigate the dependence on the gauge origin, we ran the phase-space electronic Hamiltonian calculations with a distributed origin gauge. That being said, we still found that we required a large basis for the calculations to match the experiment.

With this background in mind, if we seek to improve our phase-space approach, one means to address this dependence on origin is to implement the formalism above and evaluate the electronic energy using GIAOs (that eliminate any gauge dependence for E_{PS}) and to perform the substitution:

$$\frac{\partial m^e_\beta}{\partial P_{\mathrm{A}\alpha}} = -\frac{\partial}{\partial P_{\mathrm{A}\alpha}}\left(\frac{\partial E_{\mathrm{PS}}}{\partial B_\beta}\right) = -\frac{\partial}{\partial B_\beta}\left(\frac{\partial E_{\mathrm{PS}}}{\partial P_{\mathrm{A}\alpha}}\right) \tag{61}$$

Because E_{PS} is invariant to gauge origin by construction, the resulting VCD signal must then be independent of origin as well. Ideally, such an approach should also converge easily for smaller basis sets, although this remains to be proven. Clearly, implementing such a formalism is one of our most immediate goals in the near term.

Finally, let us turn to the implications of the present results insofar as the future of phase-space electronic structure Hamiltonians. We can imagine two important avenues. First, the presence of the extra terms in a phase-space electronic Hamiltonian (eq 27), compared with a BO electronic Hamiltonian (eq 4) should have consequences for dynamics and not just for spectroscopy. Most importantly, we imagine that consequences may well arise in the context of electron transfer with spin degrees of freedom. As discussed in Section 1.2, normal BO dynamics do not conserve the total angular or linear momentum of a composite system of nuclei and electrons (and potentially spins). In the context of electron transfer, however, one can easily imagine a paradox: When an electron moves from donor to acceptor, there must be some change in electronic momentum, which must be balanced by another form of momentum (for total momentum conservation). In the context of linear momentum, that extra electronic linear momentum must be balanced by nuclear linear momentum; in the context of angular momentum, however, that extra electronic angular momentum can be balanced by either spin or nuclear angular momentum. Thus, there is the possibility that the current phase-space electronic structure picture will lead to spin-dependent electron transfer dynamics and function as one potential framework for understanding recent experiments in CISS.[4−6,9,10] Note that, in Sections 2.4 and 2.5 above (and Appendix D below), we have consistently used the fact that, at equilibrium, $\boldsymbol{P}_{\mathrm{eq}} = \dot{\boldsymbol{R}}_{\mathrm{eq}} = 0$, but this is guaranteed to be true only in the absence of SOC; thus, in the presence of SOC, one can indeed anticipate new and exciting physics.

Second, because the phase-space electronic structure Hamiltonian depends on nuclear momentum (or really velocity), one must wonder if the current formalism will offer a new approach toward modeling superconductivity. After all, it has been well-documented that, for many superconductors,[70,71] the critical temperature depends sensitively on phonons and, in particular, the mass of the nuclear isotope. Furthermore, intuitively, the extra term in the kinetic energy in eq 25 reflects the energetic consequences of the fact that, whenever a nuclear charge moves, that charge carries an orbital. Thus, whenever a nucleus is attracted to and moves toward an electron, by default, that motion induces a slight attraction between the electron carried by the nucleus and the electron to which the nucleus is attracted. This state of affairs would seem to capture some of the essence of superconductivity, and further work in this vein would appear appropriate. One must wonder if, e.g., the presence of extra terms in a phase-space electronic Hamiltonian can strongly change the nature of the electron−electron correlation problem and, e.g., induce Cooper pairing.[72]

Overall, phase-space electronic Hamiltonians would appear to be a very promising technique for future explorations in quantum chemistry, quantum dynamics, and beyond.

■ APPENDIX A. DEPENDENCE ON THE GAUGE ORIGIN

Quite generally, CD spectra (and we find especially VCD spectra) can depend sensitively on where one chooses the origin of the magnetic field operator in eqs 48 and 49. In the interest of transparency, note that our naive phase-space method will suffer from a magnetic origin problem as well; this stands in contrast to MFP, SOS, and NVP calculations, where one can show that given an infinite basis, the rotational strength will be gauge-invariant. To explain why this is so, we will now review the Stephens original work on the gauge dependence of the rotational strength[73] and comment on its implications for phase-space methods.

To begin our discussion, consider how $\boldsymbol{m}$ changes under the origin transformation $O' = O + \mathbf{Y}$. Unsurprisingly, $\boldsymbol{m}$ transforms much like angular momentum.

$$\begin{aligned}(\boldsymbol{m}^e)^O &= (\boldsymbol{m}^e)^{O'} - \frac{e}{2m_e}(\mathbf{Y} \times \langle\hat{\boldsymbol{p}}\rangle)\\ (\boldsymbol{m}^n)^O &= (\boldsymbol{m}^n)^{O'} + \sum_B \frac{Z_{\mathrm{B}}e}{2M_{\mathrm{B}}}(\mathbf{Y} \times \mathbf{P})\end{aligned} \tag{62}$$

Calculating $\frac{\partial m_\beta}{\partial P_{\mathrm{A}\alpha}}$ as before, we find

$$\frac{\partial m^O_\beta}{\partial P_{\mathrm{A}\alpha}} = \frac{\partial m^{O'}_\beta}{\partial P_{\mathrm{A}\alpha}} + \frac{-e}{2m_e}\sum_{\gamma\delta}\epsilon_{\beta\gamma\delta}Y_\gamma\frac{\partial\langle\hat{p}_\delta\rangle}{\partial P_{\mathrm{A}\alpha}} + \sum_{\mathrm{B}\gamma\delta}\frac{Z_{\mathrm{B}}e}{2M_{\mathrm{B}}}\epsilon_{\beta\gamma\delta}Y_\gamma\frac{\partial P_{\mathrm{B}\delta}}{\partial P_{\mathrm{A}\alpha}} \tag{63}$$

$$= \frac{\partial m^{O'}_\beta}{\partial P_{\mathrm{A}\alpha}} + \frac{1}{2M_{\mathrm{A}}}\sum_{\gamma\delta}\left(-e\epsilon_{\beta\gamma\delta}Y_\gamma\frac{\partial\langle\hat{r}_\delta\rangle}{\partial R_{\mathrm{A}\alpha}} + eZ_{\mathrm{A}}\epsilon_{\beta\gamma\delta}Y_\gamma\delta_{\delta\alpha}\right) \tag{64}$$

$$= \frac{\partial m^{O'}_\beta}{\partial P_{\mathrm{A}\alpha}} + \frac{1}{2M_{\mathrm{A}}}\sum_{\gamma\delta}\epsilon_{\beta\gamma\delta}Y_\gamma\frac{\partial\mu_\delta}{\partial R_{\mathrm{A}\alpha}} \tag{65}$$

In the first step, we have used the equivalent of Ehrenfest's theorem highlighted by Nafie in the context of BO theory, namely the fact that $\langle\hat{\boldsymbol{p}}\rangle = m\,(\mathrm{d}\langle\hat{\boldsymbol{r}}\rangle/\mathrm{d}t)$, which allows us to write

$$\begin{aligned}\frac{\partial\langle\hat{\boldsymbol{p}}\rangle}{\partial P_{\mathrm{A}\alpha}} &= m_e\frac{\partial}{\partial P_{\mathrm{A}\alpha}}\frac{\partial\langle\hat{\boldsymbol{r}}\rangle}{\partial t}\\ &= \frac{\partial}{\partial P_{\mathrm{A}\alpha}}\sum_{\mathrm{A}\alpha}\frac{m_e}{M_{\mathrm{A}}}\frac{\partial\langle\hat{\boldsymbol{r}}\rangle}{\partial R_{\mathrm{A}\alpha}}M_{\mathrm{A}}\dot{R}_{\mathrm{A}\alpha}\\ &= \frac{m_e}{M_{\mathrm{A}}}\frac{\partial\langle\hat{\boldsymbol{r}}\rangle}{\partial R_{\mathrm{A}\alpha}}\end{aligned} \tag{66}$$

(see Section 3 of ref 35).

Note, however, that in the context of a phase-space electronic Hamiltonian with a Γ coupling, this condition is only approximately satisfied.[35] That being said, if we invoke Nafie's approximation and we insert eq 63 into eq 57 for the rotational strength, we find

$$\mathcal{R}_k^{O'} = \sum_{A\alpha,A'\alpha'} \sum_{\beta} \frac{\hbar M_A}{2} \mathcal{S}_{A\alpha,k} \mathcal{S}_{A'\alpha',k} \frac{\partial \mu_\beta}{\partial R_{A'\alpha'}} \frac{\partial m_\beta^{O'}}{\partial P_{A\alpha}}$$
$$= \sum_{A\alpha,A'\alpha'} \sum_{\beta} \frac{\hbar M_A}{2} \mathcal{S}_{A\alpha,k} \mathcal{S}_{A'\alpha',k} \frac{\partial \mu_\beta}{\partial R_{A'\alpha'}} \times \left(\frac{\partial m_\beta^{O}}{\partial P_{A\alpha}} + \frac{1}{2M_A} \sum_{\gamma\delta} \epsilon_{\beta\gamma\delta} Y_\gamma \frac{\partial \mu_\delta}{\partial R_{A\alpha}} \right)$$
$$= \mathcal{R}_k^{O} + \sum_{A\alpha,A'\alpha'} \sum_{\beta} \hbar \mathcal{S}_{A\alpha,k} \mathcal{S}_{A'\alpha',k} \sum_{\gamma\delta} \epsilon_{\beta\gamma\delta} Y_\gamma \frac{\partial \mu_\beta}{\partial R_{A'\alpha'}} \frac{\partial \mu_\delta}{\partial R_{A\alpha}} \tag{67}$$

Note that when $\boldsymbol{Y}$ is some constant vector, $\mathcal{R}_k^{O'} = \mathcal{R}_k^{O}$:

$$\mathcal{R}_k^{O'} = \mathcal{R}_k^{O} + \sum_{\gamma\delta\beta} \epsilon_{\beta\gamma\delta} Y_\gamma \frac{\partial \mu_\beta}{\partial Q_j} \frac{\partial \mu_\delta}{\partial Q_j}$$
$$= \mathcal{R}_k^{O} + \left(\mathbf{Y} \cdot \frac{\partial \boldsymbol{\mu}}{\partial Q_j} \times \frac{\partial \boldsymbol{\mu}}{\partial Q_j} \right)$$
$$= \mathcal{R}_k^{O} \tag{68}$$

Now, the theory above is exact provided that Nafie's relationship in eq 66 holds. More generally, however, such a relationship holds only in an infinite (complete) basis. Therefore, to the extent that one always seeks to reduce dependence on basis, in the literature, one usually uses a distributed gauge origin (DO), rather than a common, fixed origin (CO). Here, one imagines looping over all atoms and shifting the origin to match up with the atom under consideration. Thus, in eq 63 above, if one is considering atom A, one chooses $\boldsymbol{Y} = \mathbf{R}_A$, and calculates

$$\left(\frac{\partial m_\beta}{\partial P_{A\alpha}} \right)^{\mathrm{CO}} = \left(\frac{\partial m_\beta}{\partial P_{A\alpha}} \right)^{\mathrm{DO}} + \frac{-e}{2m_e} \sum_{\gamma\delta} \epsilon_{\beta\gamma\delta} R_{A\gamma} \frac{\partial \langle \hat{p}_\delta \rangle}{\partial P_{A\alpha}} + \sum_{B\gamma\delta} \frac{Z_B e}{2M_B} \epsilon_{\beta\gamma\delta} R_{A\gamma} \frac{\partial P_{B\delta}}{\partial P_{A\alpha}} \tag{69}$$

Thereafter, if one again invokes Nafie's theorem, as in eq 66, one can immediately simply the second term and repeat the above procedure above to find

$$\mathcal{R}_k^{\mathrm{CO}} = \mathcal{R}_k^{\mathrm{DO}} + \sum_{A\alpha,A'\alpha'} \sum_{\beta} \hbar \mathcal{S}_{A\alpha,k} \mathcal{S}_{A'\alpha',k} \sum_{\gamma\delta} \epsilon_{\beta\gamma\delta} R_{A\gamma} \frac{\partial \mu_\beta}{\partial R_{A'\alpha'}} \frac{\partial \mu_\delta}{\partial R_{A\alpha}} \tag{70}$$

where

$$\mathcal{R}_k^{\mathrm{DO}} = \sum_{A\alpha,A'\alpha'} \sum_{\beta} \frac{\hbar M_A}{2} \mathcal{S}_{A\alpha,k} \mathcal{S}_{A'\alpha',k} \frac{\partial \mu_\beta}{\partial R_{A'\alpha'}} \left(\frac{\partial m_\beta}{\partial P_{A\alpha}} \right)^{\mathrm{DO}} \tag{71}$$

The second term in eq 70 (coined the $L{\cdot}P$ term by Stephens[73]) is well-known. The explicit gauge origin dependence is hidden in $\mathcal{R}_k^{\mathrm{DO}}$ and, in practice, evaluating this expression often gives much better results for an incomplete basis than simply picking the gauge origin as the center of nuclear charge. Indeed, we have found that, without this expression, our results can be very sensitive to the origin. Thus, all data gathered in this paper (for Figures 1−3) used eq 70.

■ APPENDIX B. NUCLEAR MOMENTUM CPSCF

In this section, we will present the equations needed to solve for the orbital response derivatives for the Hamiltonian given in eq 28 (i.e., how to calculate $\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{R}}$, $\frac{\partial \boldsymbol{m}}{\partial \mathbf{P}}$ in eq 59, eq 58, and the elements of $\boldsymbol{W}$, $\boldsymbol{K}$, $\boldsymbol{Y}$ in eqs 80, 79, and 81). Before embarking on such a derivation, we note that we use the following notation below for molecular orbitals:

- Roman letters a and b denote virtual molecular orbitals
- Roman letters i and j denote occupied molecular orbitals
- Roman letters p, q, and n denote all molecular orbitals

To begin our derivation, we suppose that there exists a unitary transformation of the orbital coefficients which transforms the orbital coefficients from their current value to a different value, as determined some small perturbation in the variable of interest X. This unitary transformation can be written as

$$c_{\mu q}^{[X]} = \sum_{n}^{n_{\mathrm{orb}}} c_{\mu n} U_{nq}^{[X]} \tag{72}$$

As shown by ref 74, $U^{[X]}$ can be determined by differentiating the Fock equation, with respect to X and retaining the first-order terms. Rather than solve for the entire $U^{[X]}$, because only the occupied virtual block is ultimately relevant,[74] we opt to use the antisymmetrized occupied virtual $\tilde{U}^{[X]} = \frac{1}{2}(U^{[X]} - U^{[X]\dagger})$. Carrying out the CPSCF procedure yields the matrix equation

$$A\tilde{U}^{[X]} = B^{[X]} \tag{73}$$

where A is independent of the perturbation and is given as

$$(A\tilde{U}^{[X]})_{ai} = \sum_{bj} [F_{ab}\delta_{ij} - F_{ji}\delta_{ab} + (ai\|\mathrm{jb})] \frac{1}{2} (U_{bj}^{[X]} - U_{jb}^{[X]*}) + \sum_{bj} (ai\|\mathrm{bj}) \frac{1}{2} (U_{bj}^{[X]*} - U_{jb}^{[X]}) \tag{74}$$

The form of $B^{[X]}$ does depend on the perturbation, but can generally be written as

$$B_{ai}^{[X]} = -\overline{F}_{ai}^{[X]} + \frac{1}{2} \sum_{j} \overline{S}_{aj}^{[X]} F_{ji} + \frac{1}{2} \sum_{b} F_{ab} \overline{S}_{bi}^{[X]} + \frac{1}{2} \sum_{jn} [(ai\|\mathrm{jn}) \overline{S}_{nj}^{[X]} + (ai\|\mathrm{nj}) \overline{S}_{jn}^{[X]}] \tag{75}$$

where bar matrices indicate the derivative contains only the explicit and atomic orbital derivative contributions (i.e., no MO coefficient derivatives). If the atomic orbitals have no explicit dependence on the variable of interest (i.e., $\mathbf{X} = P_{A\alpha}$), this result simplifies to

$$B_{ai}^{[P_{A\alpha}]} = -\overline{F}_{ai}^{[P_{A\alpha}]}$$
$$= -\sum_{\mu\nu\tau\kappa} c_{\mu a}^{\tau *} \langle \chi_\mu | \frac{\partial h}{\partial P_{A\alpha}} | \chi_\nu \rangle c_{\nu i}^{\kappa}$$
$$= \sum_{\mu\nu\tau\kappa} c_{\mu a}^{\tau *} \left(i\hbar \frac{\Gamma_{\mu\nu}^{A\alpha}}{M_A} \right) c_{\nu i}^{\kappa} \tag{76}$$

Solving these equations corresponds to finding the solutions to the matrix equation

$$\begin{bmatrix} F_{ab}\delta_{ij} - F_{ji}\delta_{ab} + (ai\|jb) & (ai\|bj) \\ (ai\|bj)^{*} & F^{*}_{ab}\delta_{ij} - F^{*}_{ji}\delta_{ab} + (ai\|jb)^{*} \end{bmatrix} \begin{bmatrix} \frac{1}{2}(U^{[X]}_{bj} - U^{[X]*}_{jb}) \\ \frac{1}{2}(U^{[X]*}_{bj} - U^{[X]}_{jb}) \end{bmatrix} = \begin{bmatrix} B^{[X]}_{ai} \\ B^{[X]*}_{ai} \end{bmatrix} \tag{77}$$

Finally, using the identity that $U^{[X]}_{ja}*+ U^{[X]}_{aj}+\overline{S}^{[X]}_{aj} = 0$, density derivatives are calculated as

$$D^{\tau\kappa,[X]}_{\mu\nu} = \frac{1}{2}\Bigg[\sum_{ia} c^{\tau}_{\mu a}(U^{[X]}_{ai} - U^{[X]*}_{ia})c^{\kappa *}_{\nu i} + c^{\tau}_{\mu i}(U^{[X]*}_{ai} - U^{[X]}_{ia})c^{\kappa *}_{\nu a} - \sum_{n\sigma\lambda\eta} c^{\tau}_{\mu n}c^{\eta *}_{\sigma n}S^{[X]}_{\sigma\lambda}D^{\eta\kappa}_{\lambda\nu} - D^{\tau\eta}_{\mu\sigma}S^{[X]}_{\sigma\lambda}c^{\eta}_{\lambda n}c^{\kappa *}_{\nu n}\Bigg] \tag{78}$$

APPENDIX C. COMPUTING K, W, AND Y IN EQ 40: EXPANDING THE GHF PHASE-SPACE HAMILTONIAN ENERGY TO SECOND ORDER

In this section of the Appendix, we will evaluate the matrices $\boldsymbol{K}$, $\boldsymbol{W}$, and $\boldsymbol{Y}$ in eq 40. Quite generally, the energy of a GHF wave function is given by the eq 30. Carrying out the Hartree–Fock derivatives in the standard fashion (and noting that overlap momentum derivatives vanish $S^{[P]} = 0$), yields the relatively simple expressions:

$$\frac{\partial^2 E_{\mathrm{PS}}}{\partial P_{\mathrm{A}\alpha}\partial R_{\mathrm{B}\beta}} = -i\hbar\sum_{\mu\nu\tau}\frac{\Gamma^{\mathrm{A}\alpha}_{\mu\nu}}{M_{\mathrm{A}}}(D^{\tau\tau}_{\mu\nu})^{[R_{\mathrm{B}\beta}]} - i\hbar\frac{(\Gamma^{\mathrm{A}\alpha}_{\mu\nu})^{[R_{\mathrm{B}\beta}]}}{M_{\mathrm{A}}}D^{\tau\tau}_{\mu\nu} \tag{79}$$

$$\frac{\partial^2 E_{\mathrm{PS}}}{\partial P_{\mathrm{A}\alpha}\partial P_{\mathrm{B}\beta}} = \frac{1}{M_{\mathrm{A}}}\delta_{\mathrm{AB}}\delta_{\alpha\beta} - i\hbar\sum_{\mu\nu\tau}\frac{\Gamma^{\mathrm{A}\alpha}_{\mu\nu}}{M_{\mathrm{A}}}(D^{\tau\tau}_{\mu\nu})^{[P_{\mathrm{B}\beta}]} \tag{80}$$

$$\frac{\partial^2 E_{\mathrm{PS}}}{\partial R_{\mathrm{A}\alpha}\partial R_{\mathrm{B}\beta}} = \sum_{\mu\nu\tau}\sum_{C\gamma}\Bigg[-\frac{i\hbar P_{C\gamma}}{M_C}\big((\Gamma^{C\gamma}_{\mu\nu})^{[R_{\mathrm{A}\alpha}]}(D^{\tau\tau}_{\mu\nu})^{[R_{\mathrm{B}\beta}]} + (\Gamma^{C\gamma}_{\mu\nu})^{[R_{\mathrm{A}\alpha}R_{\mathrm{B}\beta}]}D^{\tau\tau}_{\mu\nu}\big) - \frac{\hbar^2}{2M_C}\big((\tilde{\Gamma}^{C\gamma}S\tilde{\Gamma}^{C\gamma})^{[R_{\mathrm{A}\alpha}]}_{\mu\nu}(D^{\tau\tau}_{\mu\nu})^{[R_{\mathrm{B}\beta}]} + (\tilde{\Gamma}^{C\gamma}S\tilde{\Gamma}^{C\gamma})^{[R_{\mathrm{A}\alpha}R_{\mathrm{B}\beta}]}_{\mu\nu}D^{\tau\tau}_{\mu\nu}\big)\Bigg] + \left(\frac{\partial^2 E}{\partial R_{\mathrm{A}\alpha}\partial R_{\mathrm{B}\beta}}\right)_{\mathrm{eq}} \tag{81}$$

Here, $\left(\frac{\partial^2 E}{\partial R_{\mathrm{A}\alpha}\partial R_{\mathrm{B}\beta}}\right)_{\mathrm{eq}}$ is the regular BO Hessian expression.

Note that, for systems with formal time-reversal symmetry and without degeneracy or near degeneracy in the ground state, we expect that the minimum energy of the phase-space electronic Hamiltonian will occur at $\boldsymbol{P} = 0$. In such a case, the electronic wave function will be real-valued. Furthermore, note that any real function must also have real derivatives, thus, the density derivatives must also be real and $D^{[R]}_{\mu\nu}$ must be symmetric (since $D^{[R]}_{\mu\nu} = \sum_i c^{[R]}_{\mu i}c_{\nu i} + c_{\mu i}c^{R}_{\nu i} = D^{[R]}_{\nu\mu}$). At the same time, it is clear that Γ and $\Gamma^{[R]}$ are antisymmetric (as seen in Appendix F). Thus, according to eq 79, we find that $\frac{\partial^2 E_{\mathrm{PS}}}{\partial P_{\mathrm{A}\alpha}\partial R_{\mathrm{B}\beta}}$ should always be zero.

As a sidenote, exploring degenerate ground states when these simplifications would no longer hold will be extremely interesting in the future.

APPENDIX D. MAGNETIC FIELD PERTURBATION EQUIVALENCE

In this section of the Appendix, for the sake of completeness, we review MFP for the reader and show why a phase-space electronic Hamiltonian approach to a VCD spectra is equivalent to MFP[19]—if one were to include the entire derivative coupling (see eq 11), instead of Γ in the equations for $\frac{\partial m}{\partial \mathbf{P}}$. Let us begin by considering the perturbative expansion of our BO wave function using the derivative coupling as our perturbation, $H' = -i\hbar\frac{\mathbf{P}\cdot\nabla}{M}$. According to pertrubation theory, the perturbed electronic ground state can be written down as a sum over all other electronic states n:

$$\begin{aligned} |\Phi_G\rangle &= |\Phi_G\rangle_{\mathrm{eq}} + \sum_{\mathrm{A}\alpha}\left(\frac{-i\hbar}{M_{\mathrm{A}}}\sum_{n\neq G}\frac{\langle\Phi_n|\nabla|\Phi_G\rangle}{(E_G - E_n)}|\Phi_n\rangle\right)_{\mathrm{eq}} P_{\mathrm{A}\alpha} \\ &= |\Phi_G\rangle_{\mathrm{eq}} + \sum_{\mathrm{A}\alpha}\left(\frac{-i\hbar}{M_{\mathrm{A}}}\sum_{n\neq G}\frac{d^{\mathrm{A}\alpha}_{nG}}{(E_G - E_n)}|\Phi_n\rangle\right)_{\mathrm{eq}} P_{\mathrm{A}\alpha} \end{aligned} \tag{82}$$

Viewed as a Taylor expansion, eq 82 implies that

$$\left|\frac{\partial\Phi_G}{\partial P_{\mathrm{A}\alpha}}\right\rangle_{\mathrm{eq}} = \frac{-i\hbar}{M_{\mathrm{A}}}\sum_{n\neq G}\frac{d^{\mathrm{A}\alpha}_{nG}}{(E_G - E_n)}|\Phi_n\rangle \tag{83}$$

Next, if we insert our pertubative wave function into eq 56 and keep the first-order terms (keeping in mind that the zeroth-order terms vanish),

$$\begin{aligned}\left(\frac{\partial}{\partial P_{\mathrm{A}\alpha}}\langle\Phi_G|\hat{m}^e|\Phi_G\rangle\right)_{\mathrm{eq}} &= \frac{e}{2m_e}\left(\left\langle\frac{\partial\Phi_G}{\partial P_{\mathrm{A}\alpha}}\middle|\hat{\mathbf{L}}^e|\Phi_G\right\rangle + \left\langle\Phi_G|\hat{\mathbf{L}}^e\middle|\frac{\partial\Phi_G}{\partial P_{\mathrm{A}\alpha}}\right\rangle\right)_{\mathrm{eq}} \\ &= \frac{-i\hbar e}{2M_{\mathrm{A}}m_e}\sum_{n\neq G}\left(\frac{d_{Gn}^{\mathrm{A}\alpha}}{(E_G-E_n)}\langle\Phi_n|\hat{\mathbf{L}}^e|\Phi_G\rangle + \langle\Phi_G|\hat{\mathbf{L}}^e|\Phi_n\rangle\frac{d_{nG}^{\mathrm{A}\alpha}}{(E_G-E_n)}\right)_{\mathrm{eq}} \\ &= \frac{-i\hbar e}{2M_{\mathrm{A}}m_e}\times\sum_{n\neq G}\left(\frac{\langle\Phi_G|\frac{\partial\hat{H}}{\partial R_{\mathrm{A}\alpha}}|\Phi_n\rangle}{(E_G-E_n)^2}\langle\Phi_n|\hat{\mathbf{L}}^e|\Phi_G\rangle - \langle\Phi_G|\hat{\mathbf{L}}^e|\Phi_n\rangle\frac{\langle\Phi_n|\frac{\partial\hat{H}}{\partial R_{\mathrm{A}\alpha}}|\Phi_G\rangle}{(E_G-E_n)^2}\right)_{\mathrm{eq}} \\ &= \frac{-i\hbar e}{M_A m_e}\left(\sum_{n\neq G}\frac{\langle\Phi_G|\frac{\partial\hat{H}}{\partial R_{\mathrm{A}\alpha}}|\Phi_n\rangle\langle\Phi_n|\hat{\mathbf{L}}^e|\Phi_G\rangle}{(E_G-E_n)^2}\right)_{eq}\end{aligned} \tag{84}$$

where Hellman-Feynman was invoked in the third step, and, in the fourth step, we used the fact that $\hat{\boldsymbol{L}}^e$ is Hermitian and purely imaginary.

Next, we consider the Hamiltonian under some constant perturbative magnetic field. This perturbation can be written as

$$H' = -\hat{m}^e\cdot\mathbf{B} = \frac{e}{2m_e}\hat{L}^e\cdot\mathbf{B}$$

According to first-order Rayleigh perturbation theory, the first-order wave function $|\Phi_G\rangle$ becomes

$$|\Phi_G\rangle = |\Phi_G\rangle_{\mathrm{eq}} + \frac{e}{2m_e}\left(\sum_{n\neq G}\frac{\langle\Phi_n|\hat{L}^e|\Phi_G\rangle}{(E_G-E_n)}|\Phi_n\rangle\right)_{\mathrm{eq}}\cdot\mathbf{B} \tag{85}$$

Viewed as a Taylor expansion, eq 85 implies that

$$\left|\frac{\partial\Phi_G}{\partial B_\beta}\right\rangle_{\mathrm{eq}} = \frac{e}{2m_e}\left(\sum_{n\neq G}\frac{\langle\Phi_n|\hat{L}_\beta^e|\Phi_G\rangle}{(E_G-E_n)}|\Phi_n\rangle\right)_{\mathrm{eq}} \tag{86}$$

Next, if we perturb the Hamiltonian by a nuclear coordinate perturbation, $\hat{H}' = \sum_{\mathrm{A}\alpha}\left(\frac{\partial\hat{H}}{\partial R_{\mathrm{A}\alpha}}\right)_{\mathrm{eq}}\cdot(R_{\mathrm{A}\alpha} - R_{\mathrm{A}\alpha}^{\mathrm{eq}})$, we find one more relevant expression:

$$\langle\Phi_G| = \langle\Phi_G|_{\mathrm{eq}} + \sum_{\mathrm{A}\alpha}\left(\sum_{m\neq G}\frac{\langle\Phi_G|\frac{\partial\hat{H}}{\partial R_{\mathrm{A}\alpha}}|\Phi_m\rangle}{(E_G-E_m)}\langle\Phi_m|\right)_{\mathrm{eq}}\cdot(R_{\mathrm{A}\alpha} - R_{\mathrm{A}\alpha}^{\mathrm{eq}}) \tag{87}$$

or, in other words,

$$\left\langle\frac{\partial\Phi_G}{\partial R_{\mathrm{A}\alpha}}\right|_{\mathrm{eq}} = \left(\sum_{m\neq G}\frac{\langle\Phi_G|\frac{\partial\hat{H}}{\partial R_{\mathrm{A}\alpha}}|\Phi_m\rangle}{(E_G-E_m)}\langle\Phi_m|\right)_{\mathrm{eq}} \tag{88}$$

Taking the inner product of eqs 88 and 85, we find

$$\begin{aligned}\left\langle\frac{\partial\Phi_G}{\partial B_\beta}\middle|\frac{\partial\Phi_G}{\partial R_{\mathrm{A}\alpha}}\right\rangle_{\mathrm{eq}} &= \frac{e}{2m_e}\left(\sum_{n,m\neq G}\frac{\langle\Phi_G|\hat{L}_\beta^e|\Phi_m\rangle}{E_G-E_m}\frac{\langle\Phi_n|\frac{\partial H}{\partial R_{\mathrm{A}\alpha}}|\Phi_G\rangle}{E_G-E_n}\langle\Phi_m||\Phi_n\rangle\right)_{\mathrm{eq}} \\ &= \frac{e}{2m_e}\left(\sum_{n\neq G}\frac{\langle\Phi_G|\frac{\partial H}{\partial R_{\mathrm{A}\alpha}}|\Phi_n\rangle\langle\Phi_n|\hat{L}_\beta^e|\Phi_G\rangle}{(E_G-E_n)^2}\right)_{\mathrm{eq}}\end{aligned} \tag{89}$$

From eqs 84 and 89, it follows that

$$\left(\frac{\partial}{\partial P_{\mathrm{A}\alpha}}\langle\Phi_G|\hat{m}_\beta^e|\Phi_G\rangle\right)_{\mathrm{eq}} = \frac{2i\hbar}{M_{\mathrm{A}}}\left\langle\frac{\partial\Phi_G}{\partial B_\beta}\middle|\frac{\partial\Phi_G}{\partial R_{\mathrm{A}\alpha}}\right\rangle_{\mathrm{eq}} \tag{90}$$

which is the basis for the MFP VCD expression.[19]

■ APPENDIX E. ON THE CALCULATION OF $\tilde{\mathbf{\Gamma}}$ AND A PROOF THAT THE KINETIC ENERGY (EQ 25) IS POSITIVE DEFINITE

In this section, we will begin by showing how to evaluate $\tilde{\mathbf{\Gamma}}$ in eq 26 above. Starting from eq 26, we compute the unitary transformation which diagonalizes the overlap matrix S ($U^\dagger SU = s$) and

$$\begin{aligned}&\frac{1}{2}(s_\lambda(U^\dagger\tilde{\mathbf{\Gamma}}U)_{\lambda\sigma} + (U^\dagger\tilde{\mathbf{\Gamma}}U)_{\lambda\sigma}s_\sigma) = (U^\dagger\mathbf{\Gamma}U)_{\lambda\sigma} \\ &\Rightarrow \tilde{\mathbf{\Gamma}}_{\mu\nu}^A = \sum_{\sigma\lambda}2U_{\mu\sigma}((s_\lambda + s_\sigma)^{-1}(U^\dagger\mathbf{\Gamma}^A U)_{\sigma\lambda})(U^\dagger)_{\lambda\nu}\end{aligned} \tag{91}$$

Next, let us show that eq 30 is positive-definite in momentum $\boldsymbol{P}$. For simplicity, let us suppose we have a single nuclear degree of freedom. According to eq 30, the nuclear kinetic energy is of the following form:

$$\langle\hat{T}_{\mathrm{nuc}}\rangle = \frac{1}{2M}(P^2 - i\hbar\mathrm{Tr}((\tilde{\Gamma}S + S\tilde{\Gamma})D)P - \hbar^2\mathrm{Tr}((\tilde{\Gamma}S\tilde{\Gamma})D)) \tag{92}$$

Note that, in this expression, Γ, S, and D are all matrices. Now, let $D_S = S^{1/2}DS^{1/2}$, and $\Gamma_S = i\hbar S^{1/2}\,\tilde{\Gamma}S^{-1/2}$. Note that $\Gamma_S^\dagger = i\hbar S^{-1/2}\tilde{\Gamma}S^{1/2}$ and that $D_S^2 = D_S$. Under this transformation, $\langle T_{\mathrm{nuc}}\rangle$ can be rewritten as

$$\begin{aligned}\langle\hat{T}_{\mathrm{nuc}}\rangle &= \frac{1}{2M}[P^2 - \mathrm{Tr}((\Gamma_S^\dagger + \Gamma_S)D_S)P + \mathrm{Tr}(\Gamma_S^\dagger\Gamma_S D_S)]\\ &= \frac{1}{2M}[P^2 - \mathrm{Tr}((\Gamma_S^\dagger + \Gamma_S)D_S)P + \mathrm{Tr}(\Gamma_S^\dagger D_S)\mathrm{Tr}(\Gamma_S D_S)\\ &\quad +\mathrm{Tr}(\Gamma_S^\dagger\Gamma_S D_S) - \mathrm{Tr}(\Gamma_S^\dagger D_S)\mathrm{Tr}(\Gamma_S D_S)]\\ &= \frac{1}{2M}[(P - \mathrm{Tr}(\Gamma_S D_S))(P - \mathrm{Tr}(\Gamma_S^\dagger D_S)) + \mathrm{Tr}(\Gamma_S^\dagger\Gamma_S D_S)\\ &\quad - \mathrm{Tr}(\Gamma_S^\dagger D_S)\mathrm{Tr}(\Gamma_S D_S)]\\ &= \frac{1}{2M}[(P - \mathrm{Tr}(\Gamma_S D_S))(P - \mathrm{Tr}(\Gamma_S^\dagger D_S))\\ &\quad +\mathrm{Tr}(((D_S\Gamma_S)^\dagger - \mathrm{Tr}(\Gamma_S^\dagger D_S))(D_S\Gamma_S - \mathrm{Tr}(\Gamma_S D_S)))]\end{aligned} \tag{93}$$

Since both terms in this expression are squared scalars, the entire quantity must be positive definite.

APPENDIX F. EXPLICIT DEFINITIONS OF Γ FROM REFERENCE [55]

For the sake of concreteness, we will here repeat the exact definitions of $\mathbf{\Gamma}'$ and $\mathbf{\Gamma}''$ from ref 55. First, as far as $\mathbf{\Gamma}'$ is concerned, we set

$$\Gamma'^{A\alpha}_{\mu\nu} = \frac{1}{2i\hbar}p^{\alpha}_{\mu\nu}(\delta_{\mathrm{BA}} + \delta_{\mathrm{CA}}) \tag{94}$$

just as in eq 12 above. Here and below, μ indexes an orbital centered on atom B, ν indexes an orbital centered on atom C, and $p^{\alpha}_{\mu\nu}$ is the α-component of the electronic momentum. Intuitively, the electronic momentum operator emerges because we must take into account the fact that any nuclear displacement moves the electrons as well.

As far as the definition of $\mathbf{\Gamma}''$ is concerned, we set

$$\mathbf{\Gamma}''^{\mathrm{A}}_{\mu\nu} = \zeta^{\mathrm{A}}_{\mu\nu}\mathbf{X}_{\mathrm{A}} \times (\mathbf{K}^{-1}_{\mu\nu}\mathbf{J}^{\mathrm{A}}_{\mu\nu}) \tag{95}$$

$$\mathbf{K}_{\mu\nu} = -\sum_{\mathrm{A}}\zeta^{\mathrm{A}}_{\mu\nu}(\mathbf{X}_{\mathrm{A}}^{\mathrm{T}}\mathbf{X}_{\mathrm{A}})\mathbf{I} + \sum_{\mathrm{A}}\zeta^{\mathrm{A}}_{\mu\nu}\mathbf{X}_{\mathrm{A}}\mathbf{X}_{\mathrm{A}}^{\mathrm{T}} \tag{96}$$

$$\zeta^{\mathrm{A}}_{\mu\nu} = \exp\left(-w\frac{2|(\mathbf{X}_{\mathrm{A}} - \mathbf{X}_{\mathrm{B}})|^2|(\mathbf{X}_{A} - \mathbf{X}_{C})|^2}{|(\mathbf{X}_{\mathrm{A}} - \mathbf{X}_{\mathrm{B}})|^2 + |(\mathbf{X}_{\mathrm{A}} - \mathbf{X}_{\mathrm{C}})|^2}\right) \tag{97}$$

$$\boldsymbol{J}_{\mu\nu} = \frac{1}{i\hbar}\left\langle\chi_\mu\middle|\frac{1}{2}(\hat{\mathbf{L}}^{(\mathrm{B})} + \hat{\mathbf{L}}^{(\mathrm{C})}) + \hat{\mathbf{s}}\middle|\chi_\nu\right\rangle \tag{98}$$

Here, $\boldsymbol{J}_{\mu\nu}$ is the atomic orbital centered electronic angular momentum, $\hat{\boldsymbol{L}}^{(\mathrm{A})}$ is the electronic momentum around atom A, $\zeta^{\mathrm{A}}{}_{\mu\nu}$ is a weighting factor to maintain semilocality of $\mathbf{\Gamma}''$ (we set the parameter $w = 0.3$),[55] $\boldsymbol{I}$ is the 3 × 3 identity matrix, and the matrix $\boldsymbol{K}_{\mu\nu}$ is effectively the negative of a locality weighted massless moment of inertia in the vicinity of the χ_μ and χ_ν orbitals.

Obviously, $\mathbf{\Gamma}'$ and $\mathbf{\Gamma}''$ are anti-Hermitian. Moreover, if there is no spin−orbit coupling and we ignore the spin "$\hat{\mathbf{s}}$" term in eq 98, these matrices are also purely real and anti-symmetric.

APPENDIX G. DATA TABLES

Table 3 lists the experimental rotational strength of S-d_2-oxirane, compared with ab initio calculations; Table 4 lists the experimental rotational strength of R-d_2-cyclopropane,[60] compared with ab initio calculations; and Table 5 describes the experimental[62] rotational strength of S-propylene-oxide, compared with ab initio calculations.

Table 3. Experimental Rotational Strength of S-d_2-Oxirane, Compared with Ab Initio Calculations Using the Γ Couplings above or MFP[a]

Experimental		MFP/aug-cc-pvqz			Γ/aug-cc-pvqz		
Freq	$\mathcal{R}_{\mathrm{expt}}$	Freq	$\mathcal{R}$	Sign	Freq	$\mathcal{R}$	Sign
673		714	1.2		719	1.1	
754		835	16.3		839.0	11	
917	(+)	956	0.3		959.0	−2.6	×
885	(5)	978	5.5		984.0	3.5	
914	−6	1031	0.3	×	1034.0	−4.6	
961	−29	1080	−46.7		1083.0	−33.9	
1106	11	1251	9.1		1247.0	18.6	
1112	−5	1267	9.5	×	1263.0	7.1	×
1235	24	1364	13.9		1367.0	11.9	
1339	(−2.5)	1479	−2.1		1476.0	−0.8	
1397	(−15)	1560	−11.4		1560.0	−9.8	
2240	−10	2412	−16.4		2403.0	−8.8	
2254	12	2428	15.8		2419.0	12.4	
3015	−9	3291	−28.2		3256.0	−20.9	
3028	11	3295	33.6		3260.0	18.3	

[a] All bands calculated in solution, except for those in parentheses which are intensities in the gas-phase spectrum. Solution data in C_2Cl_4 for the C−H and C−D stretching modes and in CS_2 otherwise.

Table 4. Experimental Rotational Strength of R-d_2-Cyclopropane,[60] Compared with Ab Initio Calculations Using the Γ Couplings above or MFP[a]

Experimental		MFP/aug-cc-pvqz			Γ/aug-cc-pvqz		
Freq	$\mathcal{R}_{\mathrm{expt}}$	Freq	$\mathcal{R}$	Sign	Freq	$\mathcal{R}$	Sign
618		668	0.4		679	0.5	
632		683	−0.8		692	−2.6	
736		791	2.5		799	1.1	
786		850	−9.7		858	0.7	
857		926	4.3		933	−0.3	
909		1013	6.0		1020	1.8	
942	5.5	1076	0.4		1080	0.5	
1037	−15.9	1186	−5.6		1186	−3.1	
1052	28.2	1162	15.0		1165	11.2	
1087	−13.3	1221	−0.9		1216	−1.1	
1134	−42.6	1262	−17.2		1265	−11.7	
1180	3	1293	3.5		1298	3.0	
1290	10.2	1435	6.3		1435	4.9	
1338	−7.7	1491	−4.7		1491	−3.6	
		1620	0.6		1616	0.6	
2257	3.3	2426	10.1		2421	6.1	
2270	−3.7	2438	−10.5		2431	−6.6	
3012	1.4	3266	6.8		3237	3.7	
3035	4.4	3306	21.6		3276	11.1	
3041	−9.9	3308	−38.7		3279	−20.8	
3076	4.8	3345	10.6		3315	6.1	

[a] Experimental data in C_2Cl_4 solution for the C−H and C−D stretching modes and in CS_2 solution otherwise.

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Table 5. Experimental[62] Rotational Strength of S-Propylene-Oxide, Compared with Ab Initio Calculations Using the Γ Couplings above or MFP[a]

Experimental		MFP/aug-cc-pvqz			Γ/aug-cc-pvqz		
Freq	$\mathcal{R}_{\mathrm{expt}}$	Freq	$\mathcal{R}$	Sign	Freq	$\mathcal{R}$	Sign
200		227	−3.5		219	−1.3	
373		397	12.7		396	15.1	
414		442	7.3		441	5.0	
748	−21.6	851	−6.8		847	−6.5	
828		940	−7.9		937	2.5	
893	−42.8	986	−25.5		979	−18.5	
951	71.9	1070	25.4		1066	18.3	
1022	−6.7	1139	−12.5		1132	−7.7	
1130	8.1	1267	10.0		1261	3.1	
1143	−15.9	1296	2.9	×	1287	0.1	×
1165	21.4	1310	7.3		1301	10.7	
1103	−0.4	1238	10.2	×	1232	−4.7	
1262	15.6	1406	8.7		1399	1.5	
1368	−3.3	1526	−2.9		1515	−3.3	
1406	−8.4	1574	−11.0		1565	−10.1	
1444		1600	−3.1		1591	−1.3	
1456		1614	−0.2		1605	2.4	
1500	−4	1672	−8.0		1662	2.5	×
2928		3162	−1.1		3127	0.7	
2970		3217	7.0		3186	0.3	
2970		3231	−10.8		3200	−11.6	
2995		3242	14.9		3208	17.4	
2995		3261	−10.8		3228	−10.5	
3046	3.5	3325	5.5		3290	5.8	

[a] Mode assignments based on ref 67. Experimental data collected in neat liquid.

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Notes

The authors declare no competing financial interest.

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